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QUANTITATIVE ANALYSIS
(PARTS 4-9)

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QUANTITATIVE ANALYSIS

(PART 4)

ANALYSIS OF MINERALS

1. A **mineral** is an inorganic substance, of homogeneous composition, and formed by processes not artificial; therefore, minerals must be either elements or compounds. They may be prepared artificially, but the term mineral is restricted to those elements and compounds that are formed in nature. Thus, ferrous sulphate, as is well known, is generally prepared by man, but the same substance is found native, and we may say that the ordinary ferrous sulphate is an artificially prepared mineral. On the other hand, carborundum (silicon carbide) is a substance that does not occur native. Being a compound not formed by natural processes, it would therefore not be called a mineral.

It is evident that there is no sharp distinction between the analysis of minerals and of chemical compounds. Minerals, generally, are far from pure, and frequently one whose composition is theoretically very simple will actually contain enough impurities to make its analysis very complicated. The mineralogist classifies minerals largely by physical properties, and frequently two samples of the same mineral will vary very much in composition—one element may sometimes be entirely replaced by another. On the other hand, as the mineralogist depends for his classification on physical properties, it sometimes happens that different minerals will have the same composition; for example, the minerals calcite and aragonite are both calcium carbonate, and while most samples of each will contain some impurities, samples can be found of very great purity.

In the analysis of minerals it frequently happens that the most important determinations to make are not the substances that go to make up the mineral in its pure state, but impurities that may materially modify the usefulness. For example, limestone when perfectly pure is calcium carbonate, and contains no silica, but many samples contain silica, and in the analysis of limestone for some technical operations, a determination of silica is of much greater importance than a determination of carbon dioxide, which is a normal constituent. Water and organic matter are frequent impurities, and in making a complete analysis of a mineral it is often necessary to determine the amounts in which these are present.

LIMESTONE

2. Limestone is essentially calcium carbonate, but as it occurs in nature it always contains other substances. The constituents usually determined are insoluble matter (silica), oxides of iron, aluminum, calcium, and magnesium; but, in addition to these substances, the limestone always contains minute quantities of other elements, and when the stone is to be used for certain purposes the determination of phosphorus and sulphur becomes important. For the determination of the constituents usually sought, only one sample is used; but, when phosphorus and sulphur are estimated, a separate portion of the original sample is taken for each of these determinations.

As a rule the calcium and magnesium are weighed as oxide and pyrophosphate, respectively, and from these weights the corresponding amounts of the carbonates are calculated, but sometimes the calcium and magnesium are reported as oxides, and the carbon dioxide is determined in a separate portion of the sample. Although the latter method does not give so complete an idea of the composition of the stone to a person not familiar with chemistry, it is the more logical of the two, as by this method the chemist reports exactly what he finds rather than what he surmises.

CONSTITUENTS USUALLY DETERMINED

3. Determination of Silica.—Weigh 1 gram of the finely ground sample, which has been dried at about 125° in an air bath, into a porcelain dish, and add 25 cubic centimeters of water. Cover the dish with a watch glass, add slowly 15 cubic centimeters of concentrate hydrochloric acid, and warm on a water bath until effervescence has ceased. Then remove the watch glass, wash any liquid that has spattered on it back into the dish, add 5 or 6 drops of concentrate nitric acid to the solution, and evaporate to dryness. Remove the dish to a gauze or piece of sheet iron over a Bunsen burner, and heat gently until the odor of hydrochloric acid can no longer be detected and the calcium chloride just begins to fuse, but avoid excessive ignition, as this may render the oxides of iron and aluminum insoluble in hydrochloric acid, and cause the silica to partially reunite with bases. To this residue, add 6 or 8 cubic centimeters of concentrate hydrochloric acid, and warm gently till the iron salts are dissolved; then add 50 cubic centimeters of water, and heat the solution, while stirring it continuously, until it begins to boil. Allow the solution to stand a few minutes for the precipitate to settle, filter through a small ashless filter, and wash thoroughly. Fold the filter carefully around the precipitate, place them in a platinum crucible, ignite cautiously at first to burn off the paper, and afterward ignite strongly over the blast lamp. Cool in a desiccator, and weigh as "insoluble silicious matter."

If this precipitate is perfectly white, and is small in quantity, it consists entirely of silica SiO_2, and for ordinary purposes may be reported as such; but if the silicious residue is large, or is more or less colored, it contains other substances and must be treated further. The treatment necessary will depend largely upon the amount and color of the residue, and the purpose of the analysis. If the residue is only of moderate quantity, and is white, or only slightly colored, it will contain very little, if any, material, except iron and alumina, in addition to the silica, and the first method will be

sufficiently accurate. In fact, this method is sufficiently accurate for technical purposes in nearly every case. But if the residue is very large or darkly colored, other constituents may be present, and the second method is the better in this case. Probably the second method is the more accurate of the two, and should be employed whenever strict accuracy is required.

1. Moisten the precipitate of insoluble silicious matter with 3 or 4 drops of pure water, cover it with hydrofluoric acid, add a few drops of sulphuric acid, evaporate to dryness, and cautiously ignite at a gradually increasing temperature, finally heating intensely to drive off all sulphuric acid. Cool in a desiccator, and weigh. The loss in weight is the weight of silica, which is dissolved by the hydrofluoric acid and volatilized. From this, the percentage of silica SiO_2 is calculated. To the residue in the crucible, which consists almost entirely of the oxides of iron and aluminum, add 4 or 5 cubic centimeters of pure, concentrate hydrochloric acid, and heat until this is evaporated to about 1 cubic centimeter, then add 2 or 3 cubic centimeters of water, heat to boiling, and wash the contents of the crucible into the filtrate from the insoluble silicious matter. If any of the iron and alumina remain undissolved, this does not matter greatly, as they are to be separated from this solution next.

2. Mix the insoluble silicious matter in the platinum crucible with 8 or 10 times its weight of a mixture of equal parts of dry sodium and potassium carbonates, heat over a Bunsen burner until the mass begins to cake together, and then over a blast lamp, until the mass is in a state of quiet fusion. Remove the crucible containing the fusion from the flame, and while holding it in a slanting position, slowly rotate it so that the fusion will solidify well up on the sides of the crucible, and thus expose a greater surface to the action of solvents. When cool, place the crucible in a porcelain dish, add hot water, a little at a time, and apply heat until the fusion dissolves. If the fusion dissolves very slowly, hydrochloric acid may be added towards the end of the process, but it should not be added at first, as it tends to

form a gelatinous precipitate over the surface of the fusion and thus impedes, rather than hastens, solution. Either during solution, or after solution is complete, render the liquid distinctly acid with hydrochloric acid, taking care to avoid loss by spattering during effervescence, and evaporate to dryness on the water bath. Transfer the dish to a wire gauze or sheet-iron plate, and heat over a Bunsen burner at about 150°, until the hydrochloric acid is driven off, but avoid a much higher temperature. After allowing the residue to cool, add 5 cubic centimeters of concentrate hydrochloric acid, heat gently for a few minutes, then add 20 cubic centimeters of water, heat to boiling, and finally dilute to 50 cubic centimeters. Filter, wash thoroughly with hot water, and ignite in a platinum crucible in the same way that the insoluble silicious matter was ignited. Cool in a desiccator, and weigh as silica SiO_2.

The filtrate will contain iron, aluminum, calcium, and magnesium, if these were present in the silicious residue, and is to be treated in the same manner as the filtrate from the silicious matter, and the results obtained are added to the percentages found in the main solution. The two solutions are sometimes united and the analysis completed in one operation, but it is best to analyze them separately and add the results, as when united, the large amount of calcium in the main solution will invariably carry down some of the sodium and potassium salts introduced with the filtrate from the fusion, and cause much trouble, if not the loss of the analysis. The calcium and magnesium found in this portion should be reported as oxides at all events.

4. Determination of Iron and Alumina.—Heat the filtrate from the insoluble silicious matter to boiling, and slowly add ammonia, while stirring continuously, until a very slight excess has been added. If the precipitate formed is rather large and light colored, dissolve it in 1 or 2 cubic centimeters of concentrate hydrochloric acid, and reprecipitate with a very slight excess of ammonia, in order to introduce enough ammonium chloride into the liquid to hold

everything except iron and aluminum in solution. In either case, boil the solution for a few moments after all the ammonia is added, and be sure that the solution remains alkaline, but any considerable excess of ammonia must be avoided. As soon as the precipitate settles, filter, and wash thoroughly with hot water. Fold the filter around the precipitate, place them together in a platinum crucible, and ignite, gently at first, to burn off the paper, but finally at the full power of a blast lamp. Cool in a desiccator, and weigh as oxides of iron and aluminum, Fe_2O_3 and Al_2O_3. As a rule, the percentage of the two oxides is all that is required, but occasionally the percentage of each oxide is wanted. When this happens, they should be separated as directed in Art. **10.**

5. Determination of Calcium Oxide or Carbonate. If the filtrate from the iron and alumina greatly exceeds 200 cubic centimeters in volume, evaporate it to about this bulk, and to the boiling solution add 5 cubic centimeters of concentrate ammonia, then add about 35 cubic centimeters of a saturated solution of ammonium oxalate, and continue the boiling for a few moments. Enough ammonium oxalate must be added to convert all the calcium and magnesium into oxalates or the precipitation of calcium will not be complete. Stand the beaker and contents in a moderately warm place for at least 4 hours, for the precipitate to collect and settle. In the analysis of limestone for technical purposes, the solution is sometimes only allowed to stand for 15 or 20 minutes, and satisfactory results are thus obtained, but if exact results are sought, it should be allowed to stand at least 4 hours, for the last traces of calcium are only precipitated after standing for some time. Filter, and wash thoroughly with hot water containing 1 or 2 per cent. of ammonia, dry in an air bath, remove the precipitate from the filter, and burn the latter in a weighed platinum crucible. When cool, add the precipitate, heat gently for a few moments, then increase the temperature, and ignite at the full power of the blast lamp for 10 or

15 minutes. Let the preciptate cool, add 2 or 3 drops of water, and again ignite at the full power of the blast lamp for 10 minutes, after heating gently at first to expel the water. Cool in a desiccator, and weigh as soon as cool. Ignite the precipitate again for 10 minutes, cool in a desiccator, and weigh as soon as cool. If this weight is lower than the first one, the ignition must be repeated until a constant weight is obtained. The precipitate is now calcium oxide CaO, and if it is to be reported as such, no calculation is necessary. If, however, the ordinary method of reporting results is to be followed, the weight of calcium carbonate is obtained by multiplying the weight of calcium oxide by 1.7857.

If preferred, the precipitate of calcium oxalate may be converted into sulphate and weighed as such, by following the directions given under Determination of Calcium as Sulphate, or the precipitate may be washed with pure hot water, and the calcium oxide (lime) determined volumetrically as previously directed.

6. Determination of Magnesium Oxide or Carbonate.—Evaporate the filtrate from the calcium oxalate to about 250 cubic centimeters, and add about 25 cubic centimeters of a saturated solution of microcosmic salt $HNaNH_4PO_4$, while stirring continuously. Then cool the solution by standing the beaker containing it in ice water, and add about 50 cubic centimeters of concentrate ammonia, adding the first portion drop by drop while stirring continuously. After the ammonia is all added, stir several times while the precipitate is forming, but in all the stirring take care not to strike the sides or bottom of the beaker with the rod; then cover the beaker with a watch glass and stand it aside for at least 6 hours; or, better still, allow it to stand overnight. Filter, and wash the precipitate thoroughly with a solution made by mixing 150 cubic centimeters of concentrate ammonia with 350 cubic centimeters of water, and adding 50 grams of ammonium nitrate. Dry the precipitate in an air bath, remove it from the filter, and burn the

latter in a porcelain crucible. When cool, add the precipitate, and ignite intensely over the blast lamp for 10 or 15 minutes. Cool in a desiccator and weigh as magnesium pyrophosphate $Mg_2P_2O_7$, which, multiplied by .36036, gives the weight of magnesium oxide MgO; or, multiplied by .75676, gives the weight of magnesium carbonate $MgCO_3$.

CONSTITUENTS SOMETIMES REQUIRED

7. Determination of Carbon Dioxide.—If the calcium and magnesium in the limestone are calculated to carbonates, a determination of carbon dioxide is not required, but if they are reported as oxides, the carbon dioxide should be determined and its percentage reported. The following simple and rapid method yields satisfactory results if carefully performed. In fact, it is the writer's experience that after a little practice, very accurate results may be obtained by this method.

Place about 4.5 grams of borax glass in a weighed platinum crucible, heat moderately until it is in a state of quiet fusion, cool in a desiccator, and weigh. As the weight of the crucible is known, the weight of perfectly dry borax is thus obtained. If it is somewhat more than 4 grams, sufficient borax has been taken, otherwise add more and fuse again. After exactly balancing the crucible containing the borax, leave it standing on the pan of the balance; add a 1-gram weight to the weights on the other pan, and then add just enough of the powdered sample to again exactly balance it; 1 gram of the sample will thus be weighed off. Now transfer the crucible to a tripod, apply heat, gradually increasing the temperature until the crucible is heated to redness, and maintain this temperature until the contents are in a state of quiet fusion. A few bubbles of gas will always remain in the fusion, but these have no influence on the result. Cool the crucible and contents in a desiccator, and weigh. The loss in weight is the weight of carbon dioxide.

If carefully performed, this method yields very satisfactory

results, and it is commended by its simplicity, but care is necessary. If strongly ignited, the borax rapidly suffers loss, so a red heat is all that is safe to apply.

There is always a chance that other substances may be present that would be volatilized, and consequently be determined as carbon dioxide, when this method is used; hence, when absolute accuracy is required, the carbon dioxide is usually evolved by treating the sample with acid, absorbed in soda lime, and weighed directly as described under Calcium Carbonate.

8. Determination of Phosphorus.—Weigh 5 grams of the pulverized sample into a porcelain dish, add about 40 cubic centimeters of water, cover the dish, and then cautiously add 20 cubic centimeters of concentrate hydrochloric acid. As soon as the action slackens, place on a water bath, and when effervescence ceases, remove the cover and evaporate to dryness. Heat the dish very gently over a Bunsen burner, or place it in an air bath, heated to about 115°, for an hour, to render the silica anhydrous. Add 15 cubic centimeters of concentrate nitric acid to the residue, heat gently, then add 60 cubic centimeters of water, and heat to boiling. Filter, and wash with 60 or 70 cubic centimeters of hot water, receiving the filtrate and washings in a flask having a capacity of 500 or 600 cubic centimeters. Add nearly enough concentrate ammonia to neutralize the nitric acid, but leave the solution distinctly acid. Heat the solution to exactly 85°, add 50 cubic centimeters of ammonium molybdate solution, stopper the flask, and shake for 5 minutes. Then stand the flask in a moderately warm place for from 4 to 6 hours. The solution should keep a temperature of about 40°, but not above 50°. Filter, and wash the precipitate on the filter six times with water containing 2 per cent. of nitric acid.

When the washings have all run through, throw them away and place the flask in which precipitation was made under the funnel. Pour 2 or 3 cubic centimeters of concentrate ammonia on the precipitate, and immediately stir it

up by directing a fine stream of hot water from a wash bottle upon it. When water amounting to about three times the volume of the ammonia has been added in this way, allow the solution to run through into the flask. Now remove the flask, put a small beaker in its place under the funnel, run the solution around the sides of the flask to dissolve any "yellow precipitate" that may adhere to the glass, and then pour it back on to the filter and allow it to run through again. The precipitate should now be all dissolved. Add a few drops of ammonia to the filter, then pour a few cubic centimeters of water into the flask, rinse it around and pour this on the filter. Wash the flask out once more in this way, pouring the washings on the filter, and then wash the filter twice with hot water. The phosphorus will now be all in the filtrate, which should have a volume of from 30 to 50 cubic centimeters. Nearly neutralize this solution with hydrochloric acid, but leave it distinctly alkaline. Cool it by standing the beaker in ice water, and when quite cold, slowly add 10 cubic centimeters of magnesia mixture* while stirring the solution continuously. After the reagent has all been added, add one-third the volume of the solution of concentrate ammonia, and stand in a cold place for 4 or 6 hours for the precipitate to collect and settle. Filter, and wash the precipitate with a mixture of 1 part of ammonia and 3 parts of water, to each 100 cubic centimeters of which are added 3 or 4 grams of solid ammonium nitrate. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a weighed porcelain crucible. Add the precipitate, ignite 10 minutes at the highest power of the blast lamp, cool in a desiccator, and weigh as magnesium pyrophosphate $Mg_2P_2O_7$, which contains 27.93 per cent. of phosphorus, or 63.96 per cent. of phosphoric anhydride P_2O_5.

As a rule, all phosphates should be ignited in a porcelain crucible, as the phosphorus is likely to attack platinum, especially if reducing agents are present, and it is best to

* Directions for making magnesia mixture are given in the foot-note to Art. **69**, *Quantitative Analysis*, Part 1.

always follow this rule. If care is taken, however, and the precipitate is all removed from the filter, an experienced chemist may ignite this precipitate in a platinum crucible without injuring it, and this is usually done in commercial laboratories.

9. Determination of Sulphur.—Weigh 5 grams of the dry pulverized sample into a porcelain dish, cover with a watch glass, and dissolve the sample in a mixture of 15 cubic centimeters of concentrate hydrochloric acid, 5 cubic centimeters of concentrate nitric acid, and 10 cubic centimeters of water. As soon as the violent action is over, heat to boiling, and when effervescence entirely ceases, remove the cover, wash anything adhering to it into the solution, add 10 cubic centimeters of concentrate hydrochloric acid, and evaporate to dryness to expel all nitric acid, and render the silica insoluble. Moisten the residue with 1 cubic centimeter of concentrate hydrochloric acid, add 50 cubic centimeters of water, heat just to boiling, filter off any insoluble matter, and wash the precipitate with 50 or 60 cubic centimeters of hot water. Add 5 cubic centimeters of ammonium chloride to the filtrate, heat it to boiling, and precipitate the sulphur as barium sulphate, by adding 5 cubic centimeters of barium-chloride solution while stirring constantly. As soon as the reagent is all added, remove the solution to a warm place, and allow it to stand for at least 4 hours for the precipitate to collect and settle. Decant the clear liquid through the asbestos felt of a Gooch crucible that has been ignited and weighed. Add hot water to the precipitate, bring it to boiling, allow the precipitate to settle, filter through the Gooch crucible, and wash thoroughly on the felt with hot water, finally sucking as much water as possible out of the felt by means of the filter pump. Heat the crucible over a Bunsen burner, gently at first to drive off moisture, and then increase the temperature to dull redness for 5 minutes. Cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur.

If preferred, the precipitate may be collected on a filter instead of a Gooch felt. In this case, filter, and wash in the manner just described, except that a filter paper is used instead of a Gooch crucible. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and cautiously burn the latter in a weighed porcelain crucible. Moisten the ash with 2 or 3 drops of concentrate nitric acid and a drop of concentrate sulphuric acid, evaporate to dryness, and ignite to drive off all sulphuric acid. When the crucible is cool, add the precipitate, heat to dull redness for 5 minutes, cool in a desiccator, and weigh as barium sulphate $BaSO_4$.

As this precipitate is quite easily decomposed by heat, and is readily reduced, the writer prefers the use of a Gooch crucible. If a filter is used, the particles adhering to it are reduced, and sulphuric acid must be added; and when this is driven off, if not carefully done, the precipitate will again be broken up by the heat. With proper care, however, accurate results may be obtained by this method.

10. Separation of Iron and Alumina.—As a rule, all that is required is a determination of the oxides of iron and aluminum together; but occasionally, the percentage of each of these oxides is required. When this is the case, after determining the oxides together, the oxide of iron is determined separately, and this, subtracted from the combined oxides, gives the amount of alumina. Of the several methods proposed and used for this purpose, the writer prefers the following:

After determining the iron and alumina together, weigh out a fresh sample of the pulverized stone, amounting to 1 gram; place it in a porcelain dish, cover it with 25 cubic centimeters of water, slowly add 15 cubic centimeters of concentrate hydrochloric acid, and when effervescence ceases, evaporate to dryness, after adding 5 or 6 drops of concentrate nitric acid. Add from 5 to 8 cubic centimeters of concentrate hydrochloric acid to the residue, heat gently,

and mix it with a stirring rod for a few moments; then add 50 cubic centimeters of water, and heat to boiling; filter off the insoluble matter, and wash thoroughly with hot water. Heat the filtrate to boiling and precipitate the iron and alumina with a slight excess of ammonia, as in the regular analysis. As soon as the precipitate settles, filter, and wash once or twice with hot water. Dissolve the damp precipitate with the least necessary quantity of hot dilute hydrochloric acid, receiving the solution in a flask. If the precipitate is small, it is best to dissolve it all on the filter and allow the solution to run through the paper. If a few cubic centimeters of the acid do not dissolve the precipitate, pour the solution back on the paper and let it run through again; and repeat this until the precipitate is dissolved; or, if necessary, add a little fresh acid. When all is dissolved, wash the filter with water and a few more drops of hydrochloric acid, allowing the washings to run into the flask with the main solution. The solution should not amount to more than about 100 cubic centimeters. To it, add a little more granulated zinc than will be required to unite with all the free acid present—10 grams will usually be sufficient—place a small funnel in the neck of the flask, and heat it moderately, until the action is quite violent. Continue to heat gently until the acid is almost completely neutralized, but stop before basic iron salts begin to separate. Add 15 cubic centimeters of one-third-strength sulphuric acid to this solution, and after it has acted on the remaining zinc for a few moments, pour the solution, together with the zinc still undissolved, on a large folded filter, receiving the filtrate in a rather large beaker or porcelain dish. Wash the filter once by filling it with cold water and allowing it to run through, then dilute the solution to 400 or 500 cubic centimeters with cold water, and titrate at once with a standard solution of potassium permanganate. The solution must be quite cool when titrated, and, if very warm, the flask containing it should be placed in ice water before the sulphuric acid is added. If not very warm, the cold water added in washing and diluting will cool it sufficiently.

As zinc always contains a small amount of matter that will reduce permanganate, and exact results are required in this case, a correction must be made. This is done as follows:

Place a mixture of hydrochloric acid and water, having about the same volume as the solution of iron and alumina, and containing about the same amount of free acid, in a flask. Add to this exactly the same weight of zinc that was used in reducing the iron, place a small funnel in the neck of the flask, and heat it as in the case of the iron and alumina. When the hydrochloric acid is nearly neutralized, add sulphuric acid, filter, wash, dilute, and titrate with permanganate, treating this blank as nearly as possible in the same way that the solution of iron and alumina was treated. The volume of permanganate used by the blank, subtracted from the amount used in titrating the solution of iron and aluminum, gives the volume used in oxidizing the iron, and from this, the weight of iron in the sample is calculated. The weight of iron oxide Fe_2O_3 is readily calculated from the weight of iron, and this weight, subtracted from the weight of the combined oxides, gives the weight of alumina Al_2O_3.

ZINC BLENDE

11. Zinc blende is essentially the sulphide of zinc, but it always contains more or less impurity. The foreign matter clinging to the outside of the sample—known as gangue—may consist of silica alone, or may be a silicious mixture. In addition to silica, zinc blende frequently contains small quantities of lead, cadmium, copper, iron, and manganese as impurities. The method to be employed in analyzing zinc blende depends largely upon the purpose of the analysis and the composition of the sample, and a careful qualitative examination should be made before the quantitative analysis is commenced. If only silica and zinc sulphide are present, the analysis is short and simple, while the presence of each of the impurities lengthens and complicates it.

WHEN SILICA IS THE ONLY IMPURITY

12. Determination of Silica.—Grind somewhat more than a gram of the substance to a fine powder, dry it in an air bath heated to 100° for an hour, and allow it to cool in a desiccator. Weigh 1 gram of this dry sample into a beaker or porcelain dish, cover it with a watch glass, and add fuming nitric acid drop by drop. After the acid has acted for some time in the cold, heat on the water bath until red fumes are no longer given off, then remove the watch glass, wash any particles that may have spattered on to it back into the dish with the least necessary quantity of water, and evaporate to dryness. Moisten the residue with concentrate hydrochloric acid, and again evaporate to dryness on the water bath. Add about 2 cubic centimeters of concentrate hydrochloric acid to the residue, pour on about 100 cubic centimeters of hot water, and boil for a few minutes over a Bunsen burner, to dissolve all of the zinc. Allow the insoluble matter to settle, filter, and wash well on the paper with hot water. Wrap the filter around the precipitate, place it in a platinum crucible, and ignite gently at first to expel the moisture and burn the paper, but finally ignite intensely over the blast lamp for a few minutes. Cool in a desiccator, and weigh as silica SiO_2.

13. Determination of Zinc.—Heat the filtrate from the silica to boiling in a porcelain dish, and to this gently boiling solution, add sodium carbonate, drop by drop, while stirring continuously, until the reaction of the liquid is distinctly alkaline. Continue the boiling for 5 or 10 minutes, allow the precipitate to completely subside, and pour the clear liquid through a filter. Add 50 or 60 cubic centimeters of hot water to the precipitate, heat it to boiling, allow the precipitate to settle, filter, using the paper through which the clear liquid was poured, and wash thoroughly with hot water. Dry the precipitate, remove it as completely as possible from the filter, and cautiously burn the latter in a porcelain crucible. When cool, add the precipitate and ignite gently at first, but gradually increasing the temperature to the

highest power of the Bunsen burner, or ignite moderately over a blast lamp. Cool in a desiccator, and weigh as zinc oxide ZnO, which contains 80.25 per cent. of zinc.

It may be mentioned at this point, that if iron is the only impurity besides the silica, this method may be employed, and the iron, which will be precipitated with the zinc, may be determined in this precipitate. If this is done, dissolve the precipitate containing the oxides of zinc and iron by digesting it on a water bath with concentrate hydrochloric acid. Reduce the iron in this solution with stannous chloride, and titrate with standard potassium bichromate, following the directions given under the bichromate method. From the weight of iron thus obtained, calculate the weight of ferric oxide, and subtract this weight from the weight of the mixed oxides, before calculating the percentage of zinc.

14. Determination of Sulphur.—Evaporate the filtrate and washings from the zinc precipitate to about 200 cubic centimeters after rendering slightly acid with hydrochloric acid, and to this gently boiling solution add a slight excess of barium-chloride solution, while stirring continuously. Continue the boiling for a few moments after all the reagent has been added, and then stand on a water bath, or some equally warm place, for 4 or 5 hours for the precipitate to settle and become more dense. Filter, and wash thoroughly on the filter with hot water. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a porcelain crucible. When cool, moisten the ash with a drop of concentrate sulphuric acid, and heat, gently at first, but gradually increase the temperature to dull redness to expel the excess of acid. After allowing the crucible to cool, add the precipitate and again ignite, gradually increasing the heat until the crucible assumes a dull-red color, and hold it at this temperature for 10 minutes. Allow the crucible and precipitate to cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur. From this, calculate the percentage of sulphur in the sample.

WHEN OTHER IMPURITIES ARE PRESENT

15. Determination of Insoluble Matter.—Weigh 1 gram of the dry, finely powdered sample into a porcelain dish, cover it with a watch glass, moisten it with a few drops of cold water, and then cautiously add fuming nitric acid, drawing the cover aside slightly. When violent action ceases, place on the water bath and heat with the cover on until red vapors are no longer given off. Then remove the watch glass, wash the particles that have spattered on it back into the dish, and evaporate to dryness. Moisten the residue with a little concentrate hydrochloric acid, heat it for a few minutes on the water bath, then add about 100 cubic centimeters of water, and heat to boiling. Allow the insoluble matter to settle, decant the clear liquid through a filter, and wash once by decantation with 40 or 50 cubic centimeters of boiling water. If the sample contains lead, wash the insoluble matter four times by decantation with a hot solution of ammonium acetate. This is made by adding strong acetic acid to concentrated ammonia until the liquid is acid. Then bring the precipitate on the paper and wash with hot water. Fold the filter around the precipitate, place in a platinum crucible, and ignite gently at first, but finally heat strongly over a blast lamp. Cool in a desiccator, and weigh as insoluble silicious matter or gangue.

16. Determination of Lead.—If the sample contains lead, add about 20 cubic centimeters of one-third-strength sulphuric acid, evaporate and heat until all the nitric and acetic acids are expelled. To the residue, add about 100 cubic centimeters of hot water, and, while heating on the water bath, stir with a glass rod until the precipitate appears perfectly white. Then stand aside in a rather warm place for the precipitate to completely settle. When the supernatant liquid has become perfectly clear, filter, and wash the precipitate several times with water containing 2 per cent. of sulphuric acid. Then remove the filtrate to a place of safety, set something under the funnel to catch the washings, and

wash the sulphuric acid out of the precipitate and filter with one-third-strength alcohol. These alcoholic washings may be thrown away. Dry the precipitate in an air bath, remove it as completely as possible from the paper, and cautiously burn the latter in a porcelain crucible. Moisten the ash with a drop of nitric acid and a drop of sulphuric acid, evaporate to dryness, and ignite gently to expel the excess of acid. When the crucible becomes cool, add the main precipitate, and ignite to dull redness for 5 minutes over a Bunsen burner. Cool in a desiccator, and weigh as lead sulphate $PbSO_4$.

17. Determination of Copper.—Evaporate the filtrate from the lead sulphate to from 100 to 150 cubic centimeters, or, if the sample does not contain lead, heat the filtrate from the insoluble matter to boiling. In either case, lead a rather rapid current of hydrogen sulphide through the gently boiling solution until the copper and cadmium are completely precipitated as sulphides and the precipitate settles rapidly. As soon as the precipitate settles, filter, and wash as rapidly as possible with water containing some hydrogen sulphide, protecting the precipitate from the air as much as possible to prevent oxidation.

Stand the filtrate aside for further examination and place a clean beaker under the funnel. Break the apex of the filter with a glass rod, and wash the precipitate into the clean beaker placed under the funnel, with about 30 cubic centimeters of a solution consisting of 1 part of concentrate sulphuric acid and 5 parts of water. In washing the precipitate from the filter, it is best to use a wash bottle with a very small tip in order to avoid using more than about 30 cubic centimeters of the acid mixture. When the precipitate is all washed into the beaker, cover it with a watch glass to prevent evaporation, and heat the mixture to boiling over a Bunsen burner. After boiling for a few moments, remove it from the flame and digest for an hour on a water bath. If any considerable quantity of the solution evaporates during this treatment, add sufficient water to replace that

driven off by the heat. Acid of this strength will completely dissolve the cadmium sulphide, but does not attack the sulphide of copper. After digesting for at least an hour on the water bath, filter off the copper sulphide, and wash it with pure water at first, and then with water containing hydrogen sulphide, taking care to expose the precipitate as little as possible to the action of air. Dry the precipitate in an air bath, remove it from the filter, and burn the latter in a Rose crucible. Add the precipitate, together with a little powered sulphur, and ignite in a current of pure hydrogen as directed under Determination of Copper as Sulphide. Allow the precipitate to cool in a current of hydrogen, and weigh as cuprous sulphide Cu_2S.

18. Determination of Cadmium.—Dilute the acid filtrate from the copper sulphide to about 200 cubic centimeters, heat it on a water bath, and after it has assumed about the temperature of the bath, lead a rather rapid current of hydrogen sulphide through it until the cadmium is completely precipitated as sulphide, and the solution is thoroughly saturated with the gas. As soon as the precipitate settles, filter through a filter that has previously been dried in the air bath at 105°, for an hour, and weighed. Wash the precipitate at first with hydrogen-sulphide water that has been slightly acidulated with hydrochloric acid, and then with pure water. Dry the precipitate and filter in an air bath at 105° until a constant weight is obtained. This weight, minus the weight of the dry filter, is the weight of cadmium sulphide CdS.

19. Determination of Iron.—Boil the filtrate from the mixed sulphides of copper and cadmium, until the hydrogen sulphide has been completely expelled; then add sufficient concentrate nitric acid to oxidize the iron, and continue the boiling until the iron is completely oxidized. When the solution has become cool, neutralize it with a concentrate solution of sodium carbonate, stirring the solution continuously while adding the carbonate drop by drop until a slight permanent precipitate is formed. Then add 1 or 2 drops of

concentrate hydrochloric acid, and stir the solution for 2 or 3 minutes. If this does not dissolve the precipitate, add another drop of hydrochloric acid and again stir for 2 or 3 minutes. The precipitate must all be dissolved, but the solution should be kept as near neutral as possible. To this solution add a slight excess of sodium acetate, and boil it for a few moments, when the iron will be precipitated as basic ferric acetate, while the manganese and zinc remain in solution. As soon as the precipitate settles, filter it off and wash three or four times with hot water. If the iron precipitate is of any considerable size, it will almost invariably contain some manganese and zinc, and these must be removed. To do this, dissolve the partially washed precipitate in hot dilute hydrochloric acid, wash the filter well, heat the solution to boiling, and precipitate the iron with a slight excess of ammonia. Filter as quickly as possible, and wash the precipitate thoroughly with hot water. This filtrate will contain the manganese and zinc carried down with the iron, and is added to the main filtrate for further treatment.

Fold the filter around the precipitate, place them in a platinum crucible, and ignite gently at first, but gradually increase the temperature, and finally heat intensely over the blast lamp for 5 or 10 minutes. Cool in a desiccator, and weigh as ferric oxide Fe_2O_3.

20. Determination of Zinc.—If the addition of the second filtrate to the main filtrate produces a precipitate, dissolve it in a few drops of hydrochloric or acetic acid, and evaporate the combined filtrates to about 200 cubic centimeters. Slowly add sodium carbonate to this solution, while stirring it, until a permanent precipitate forms. Dissolve this in acetic acid, adding the latter until the reaction of the solution is decidedly acid. Heat the solution until it just begins to boil, and lead a rather rapid current of hydrogen sulphide through the gently boiling solution until the zinc is completely precipitated. Half an hour will usually suffice for this. As soon as the precipitate has settled, decant the clear liquid through a filter, and wash the precipitate by

decantation with hot water containing hydrogen sulphide and a little ammonium chloride. Then transfer the precipitate to the filter, and wash it with hot water containing hydrogen sulphide. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and cautiously burn the latter in a Rose crucible. When cool, add the precipitate, together with a little powdered sulphur, and ignite in a stream of pure hydrogen, gradually increasing the temperature and finally heating for 10 minutes at the highest power of a Bunsen burner, but avoiding the use of a blast lamp. Allow the precipitate to cool in a current of hydrogen passing through the crucible, and weigh as zinc sulphide ZnS.

21. Determination of Manganese.—Evaporate the filtrate from the zinc sulphide to about 150 cubic centimeters, allow it to cool slightly, add 5 cubic centimeters of ammonium chloride, and then ammonium hydrate until the solution is very slightly alkaline. Wash the solution into a flask having a capacity of about 200 cubic centimeters, and precipitate the manganese as sulphide by adding a slight excess of ammonium sulphide. If the flask is not now full up to the neck, fill it with water, insert a stopper, and stand it in a warm place for 24 hours for the precipitate to collect and settle. Filter, and wash at first with water containing ammonium sulphide and ammonium chloride, and then with water containing ammonium sulphide alone. Dry the precipitate, remove it from the filter, and burn the latter in a Rose crucible. When cool, add the precipitate, sprinkle a little powdered sulphur over it, and ignite strongly over the blast lamp in a current of hydrogen in the same way that copper sulphide is ignited (see Determination of Copper as Sulphide). Allow the precipitate to cool in a current of hydrogen, and weigh as manganous sulphide MnS.

22. Second Method for the Separation of Zinc and Manganese.—Another method of separating the zinc and manganese in this analysis, which is largely used at the present time, is as follows: Evaporate the combined filtrates

from the iron precipitation to about 150 cubic centimeters, add sodium carbonate until a permanent precipitate forms, and dissolve this in acetic acid. Then add more sodium acetate, heat the solution nearly to boiling, add a saturated solution of bromine water until the liquid has a strong yellow color, and stand it on a water bath for an hour for the manganese to separate as hydrated oxide. Enough bromine must be added so that the solution will still be colored by it at the end of the hour. Now place the beaker on a gauze over a burner and heat carefully, finally boiling to expel the bromine. Allow the precipitate to settle, filter, and wash with water, taking care not to stir up the precipitate on the filter, or it may run through. Stand the filtrate and washings aside for the determination of zinc, and place a clean beaker under the funnel. Some of the manganese precipitate will usually cling to the beaker in which the precipitation was accomplished. Dissolve this in a small amount of sulphurous acid, to which a little hydrochloric acid is added, and pour this solution over the precipitate on the filter, thus dissolving it, and allowing the solution to run through into the clean beaker placed under the funnel to receive it. If this does not completely dissolve the precipitate, add a little more sulphurous acid to which a little hydrochloric acid has been added, and, when all is dissolved, wash the filter thoroughly with water, but keep the volume of the solution as small as possible. Boil the solution to expel the sulphur dioxide, add a slight excess of a solution of sodium-ammonium phosphate, and then to the gently boiling liquid add ammonium hydrate, drop by drop, while stirring constantly. As soon as a precipitate begins to form, stop the addition of ammonia, and stir vigorously with a glass rod until the precipitate, which is curdy at first, assumes a silky, crystalline appearance. Then add another drop of ammonia and again stir until the precipitate becomes crystalline. Continue this treatment until all the manganese is precipitated as white, crystalline manganese-ammonium phosphate. Then add 5 cubic centimeters of concentrate ammonia, stir well, and immediately stand the beaker in ice water to cool the

solution. When the liquid has become quite cold, stand it aside in a cool place for at least 2 hours for the precipitate to collect and settle. Filter, and wash the precipitate with a solution made by dissolving 10 grams of ammonium nitrate in 100 cubic centimeters of water, and adding a few drops of ammonium hydrate. Dry the precipitate in an air bath, remove it to a watch glass, and burn the filter in a porcelain crucible. When cool, add the precipitate, and ignite gently at first, but gradually increase the temperature, finally heating for 10 minutes at the full power of the blast lamp. Cool in a desiccator, and weigh as manganese pyrophosphate $Mn_2P_2O_7$.

Evaporate the filtrate set aside for the determination of zinc to 150 or 200 cubic centimeters. Add a concentrate solution of sodium carbonate to this solution, while stirring it continuously, until a slight permanent precipitate is formed. Dissolve this in a slight excess of acetic acid, heat the solution to boiling, and precipitate the zinc as sulphide by conducting a rather rapid current of hydrogen sulphide through it until the zinc is all precipitated and the solution is saturated with the reagent. As soon as the precipitate settles, filter as rapidly as possible, and wash with water containing a little ammonium nitrate and hydrogen sulphide, finally washing once with water containing only hydrogen sulphide. The addition of ammonium nitrate or ammonium chloride to the wash water, to keep the zinc sulphide precipitated from a hot acetic-acid solution from running through the filter, is seldom, if ever, necessary, but it does no harm, and may as well be added as a precaution. Dry the precipitate, remove it from the filter, and burn the latter in a Rose crucible. When cool, add the precipitate, together with a little powdered sulphur, ignite in a current of hydrogen, as directed in Art. **20**, and weigh as zinc sulphide ZnS.

23. Determination of Sulphur.—Weigh 1 gram of the pulverized mineral into a porcelain dish, moisten it with a few drops of water, and cover the dish with a watch glass. Draw the watch glass a little to one side, and add fuming nitric acid, drop by drop, until the further addition of acid no

longer produces any action in the dish. After allowing the dish to stand in a cool place for an hour, place it on a water bath and heat it gently until red fumes are no longer evolved. Then add a little concentrate hydrochloric acid, remove the watch glass, washing any particles that have spattered on it back into the dish, and evaporate the solution to dryness. Moisten the residue with hydrochloric acid, add 50 or 60 cubic centimeters of water, and heat to boiling to dissolve the residue. Filter off the gangue, and wash it thoroughly on the filter with hot water. Heat the filtrate to boiling and precipitate the sulphuric acid, formed by oxidizing the sulphur, with a moderate excess of barium chloride. Continue the boiling for a few moments after the precipitation is complete, and then stand in a warm place for 2 or 3 hours for the precipitate to separate completely. When the precipitate has settled, leaving the supernatant liquid perfectly clear, filter, and wash thoroughly on the filter with hot water. Dry the precipitate, remove it to a watch glass, and burn the filter in a porcelain crucible. Add a drop of nitric, and a drop of sulphuric, acid to the ash, evaporate to dryness, and ignite cautiously to expel the excess of sulphuric acid. When cool, add the precipitate, heat to dull redness, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur. On account of the well known tendency of barium sulphate to be reduced when ignited in the presence of paper, many chemists prefer to use a Gooch crucible for this determination. Many chemists also prefer to weigh the manganese pyrophosphate in a Gooch crucible, and this may be done by an experienced chemist, but it is best for a beginner to avoid heating phosphates in platinum vesssels, as there is always danger of the phosphorus attacking the platinum and injuring it.

CHALCOPYRITE

24. Chalcopyrite is a double sulphide of copper and iron, having the composition $Cu_2S \cdot Fe_2S_3$ or $CuFeS_2$, and is generally mixed with gangue. Some samples also contain

small quantities of cobalt, nickel, manganese, and zinc, and sometimes a sample is found that, in addition to these, contains lead, bismuth, arsenic, and antimony. A quantitative analysis should always be preceded by a careful qualitative examination, and the method of analysis adopted should be made to depend upon what is thus learned of the composition of the sample. If only the constituents usually present are contained in the mineral, they may all be determined in one sample, by using the following scheme:

In any event, select a small portion of the mineral that represents the average composition of the whole, pulverize it in an agate mortar, dry it in an air bath at a temperature ranging from 100° to 105°, and cool it in a desiccator.

25. Determination of Gangue.—Weigh 1 gram of the dry pulverized sample into a porcelain dish, mix it intimately with 3 grams of powdered potassium chlorate, cover the dish with a watch glass, and slowly add 40 cubic centimeters of concentrate nitric acid. Allow the dish to stand in a cool place for a few minutes, then place it on the water bath, and allow it to digest until the sample is completely decomposed, stirring the mixture frequently, and adding a little potassium chlorate from time to time. When decomposition is complete, remove the watch glass, wash any particles that may have spattered on it back into the dish, and evaporate to dryness. Add 10 or 15 cubic centimeters of concentrate hydrochloric acid to the residue, evaporate to dryness, and repeat the evaporation with concentrate hydrochloric acid two or three times. Moisten the dry residue with concentrate hydrochloric acid, add from 75 to 100 cubic centimeters of hot water, heat to boiling for a few moments, and filter off the insoluble matter as soon as it has settled. Wash thoroughly on the filter with hot water, wrap the paper around the precipitate, place it in a platinum crucible, ignite strongly over a blast lamp, cool in a desiccator, and weigh as insoluble matter or gangue.

26. Determination of Sulphur.—Heat the filtrate from the gangue to boiling, and precipitate the sulphuric

acid, formed by the oxidation of the sulphur, by slowly adding a solution of barium chloride in slight excess, while stirring the solution continuously. Continue the boiling for a few moments after a sufficient quantity of the reagent has been added, and then stand the beaker in a warm place for 3 or 4 hours for the precipitate to collect and settle. Filter, and wash the precipitate thoroughly with hot water. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a porcelain crucible. Moisten the ash with a drop of nitric acid and a drop of sulphuric acid, and ignite gently to drive off the excess of acid. When the crucible becomes cool, add the precipitate, heat to dull redness over a Bunsen burner, cool in a desiccator, and weigh as barium sulphate $BaSO_4$. From this weight, calculate the percentage of sulphur in the sample.

27. Determination of Copper.—Before precipitating the copper, the excess of barium chloride should be removed from the solution. To do this, heat the filtrate from the barium sulphate to boiling, and if the volume of the solution amounts to more than about 200 cubic centimeters, the boiling should be continued until the solution is reduced to about this amount. Then slowly add dilute sulphuric acid in slight excess to the boiling solution while stirring it continuously, and continue the boiling for a few moments after the reagent has all been added. Stand the solution in a warm place for a few hours for the precipitate to collect and settle; filter, and wash on the filter with hot water. The precipitate contains the excess of barium added to the solution, and may be thrown away.

Evaporate the filtrate to about 150 cubic centimeters, and, while keeping it as near the boiling point as possible, pass a moderately rapid current of pure hydrogen sulphide through it until the copper is completely precipitated as sulphide. As soon as the precipitate has settled, filter, and wash rapidly with water containing hydrogen sulphide, avoiding exposure to the air as much as possible. Dry the precipitate in an air bath, remove it to a watch glass, and

burn the filter in a Rose crucible. When the crucible is cool, add the precipitate, together with a little powdered sulphur, and ignite in a current of hydrogen. Allow the precipitate to cool in a current of hydrogen, and weigh as cuprous sulphide Cu_2S. From this weight, calculate the percentage of copper in the sample.

28. Determination of Iron.—Boil the filtrate from the copper sulphide until the hydrogen sulphide is completely expelled, add a little concentrate nitric acid, and continue the boiling until the iron is all oxidized to the ferric condition. Add about 15 cubic centimeters of ammonium chloride to the solution, and then slowly add ammonium hydrate in slight excess while stirring continuously. Continue the boiling for a moment after the precipitation is complete, then remove from the burner, and filter as soon as the precipitate has nearly settled. Wash the precipitate thoroughly on the filter with hot water, wrap the paper around it, place in a platinum crucible, heat gently at first to drive off the water and burn the paper, and then ignite strongly over a blast lamp. Cool in a desiccator, weigh as ferric oxide Fe_2O_3, and from this weight, calculate the percentage of iron in the sample.

The constituents already mentioned are the only ones contained in many samples, and in such cases the analysis is, of course, complete when this point is reached. Other samples, however, contain weighable quantities of zinc, cobalt, nickel, and manganese, and when the qualitative examination shows the presence of these, the analysis must be extended to include them.

29. Determination of Zinc.—Evaporate the filtrate from the iron precipitate to 100 or 150 cubic centimeters, add a strong solution of sodium acetate, and then acetic acid until the solution has a strong acid reaction. Heat the liquid to boiling, and while hot, pass a rather rapid current of hydrogen sulphide through it, thus precipitating the zinc, nickel, and cobalt, while the manganese remains in solution. As soon as the precipitate settles, filter, wash rapidly and

well with water containing hydrogen sulphide, and stand the filtrate aside for the determination of manganese. Dry the precipitate, remove it to a beaker, and burn the filter. Add the ash to the precipitate in the beaker, dissolve this in a little aqua regia, and evaporate the solution to dryness. Moisten the residue with hydrochloric acid and dissolve it in water. Add sodium carbonate to this solution drop by drop until a slight permanent precipitate forms, and dissolve this by adding a drop or two of hydrochloric acid, taking care to render the solution only faintly acid. Through this cold solution, lead a rather rapid current of hydrogen sulphide so long as the precipitate forms; then add a few drops of dilute sodium acetate, and continue to lead hydrogen sulphide into the solution until it is saturated with the gas.

During the precipitation of the zinc as sulphide, enough hydrochloric acid may be set free to prevent complete precipitation. When sodium acetate is added, hydrochloric acid unites with the sodium, forming sodium chloride, and setting free acetic acid, thus allowing the remaining portion of the zinc to be precipitated. Care must be taken not to add enough sodium acetate to unite with all the hydrochloric acid, or the cobalt and nickel will be precipitated as sulphides with the zinc.

After saturating the solution with hydrogen sulphide, cover the beaker and allow it to stand for 10 or 12 hours. If the directions have been carefully followed up to this point, the zinc will now be completely precipitated as sulphide, while the cobalt and nickel will remain in solution. Filter, and wash thoroughly with water containing hydrogen sulphide. Dry the precipitate in an air bath, remove it to a watch glass, and burn the filter in a Rose crucible. When the crucible is cool, add the precipitate, together with a little powdered sulphur, and ignite over a Bunsen burner in a current of hydrogen. Allow the precipitate to cool in a current of hydrogen, and weigh as zinc sulphide ZnS.

30. Determination of Cobalt.—Add a few drops of hydrochloric acid to the filtrate from the zinc sulphide, and

boil it till the hydrogen sulphide is expelled and the liquid is reduced to a small volume. Add a strong solution of potassium hydrate until the solution is slightly alkaline, render it slightly acid with acetic acid, then add a strong solution of potassium nitrite acidulated with acetic acid, and stand in a warm place for 24 hours for the precipitate of potassium-cobalt nitrite to separate. Filter, and wash the precipitate with a 10-per-cent. solution of potassium acetate to which a little potassium nitrite is added. Dry the precipitate in an air bath, and when dry, remove it to a porcelain dish. Burn the filter, and add the ash to the precipitate in the dish. Dissolve the precipitate in the least necessary quantity of hydrochloric acid, add a little water, heat the solution to boiling, precipitate the cobalt with a slight excess of sodium hydrate, and continue the boiling until the precipitate becomes dark colored, and of uniform texture. After allowing the precipitate to settle, filter, and wash thoroughly with hot water. Wrap the filter around the precipitate and ignite cautiously to burn off the paper. After the crucible has become cool, place the cover on it, lead in hydrogen until the air is all expelled, ignite in a current of hydrogen, and weigh as metallic cobalt.

31. Determination of Nickel.—Acidify the filtrate from the potassium-cobalt nitrite with hydrochloric acid, and boil it to expel the nitrous acid. Add ammonia to the solution until it is slightly alkaline, and then add acetic acid until it is just acid. Now add a few cubic centimeters of a strong solution of sodium acetate, heat to boiling, and conduct a rather rapid current of hydrogen sulphide into the boiling solution for 10 or 15 minutes. The nickel should now be completely precipitated as sulphide, and will settle rapidly. After allowing the precipitate to partially subside, add a strong solution of hydrogen sulphide to the clear supernatant liquid. If this produces a dark coloration, the nickel is not completely precipitated, and more hydrogen sulphide must be led into the solution to complete the precipitation. If no coloration is produced by the hydrogen-sulphide

solution, the precipitation is complete. In this case, as soon as the precipitate settles, filter, and wash well on the filter with water containing hydrogen sulphide, taking care to protect the precipitate from the action of air as much as possible. Dry the precipitate in an air bath, remove it to a beaker, burn the filter in a porcelain crucible, and add the ash to the precipitate. Digest the latter on a water bath with aqua regia, until the nickel sulphide is completely dissolved, and the separated sulphur appears pure yellow. Evaporate most of the excess of acid, dilute the solution with a small amount of water, and filter into a porcelain dish to remove the sulphur. Heat this solution to boiling, and precipitate the nickel with an excess of sodium hydrate. After a few moments, add bromine water a few drops at a time, while stirring constantly, until the precipitate becomes dark brown or black, and of uniform texture, taking care to keep the solution alkaline all the time. After allowing the precipitate to settle, filter, and wash thoroughly with hot water. Dry the precipitate, remove it as completely as possible from the filter, and burn the latter in a porcelain crucible. Add a drop or two of concentrate nitric acid to the ash, and evaporate to dryness. Then add the precipitate, ignite strongly, cool in a desiccator, and weigh as nickel oxide NiO.

32. Determination of Manganese.—Boil the filtrate from the mixed sulphides of zinc, cobalt, and nickel, to expel the hydrogen sulphide. Add sodium carbonate until the solution has an alkaline reaction, then render it slightly acid with acetic acid, and add a few cubic centimeters of a strong solution of sodium acetate. Heat this solution nearly to boiling, add a saturated solution of bromine water until the liquid has a strong yellow color, and heat it on the water bath for an hour. Then heat the solution over a Bunsen burner, finally boiling off the excess of bromine. Allow the precipitate to settle, filter, and wash thoroughly with hot water containing 1 per cent. of hydrochloric acid, directing the jet of water around the top of the filter and taking care

not to stir up the precipitate, or it may run through. Dry the precipitate, remove it as completely as possible from the filter, and burn the latter in a platinum crucible. Add the precipitate, ignite strongly for some time with the crucible uncovered, cool in a desiccator, and weigh as manganous-manganic oxide Mn_3O_4.

This method of determining manganese is quite largely used at the present time, and probably yields satisfactory results if only very small quantities of the metal are to be determined. If the manganese precipitate is large, however, it is very difficult to wash all of the alkali salts out of it, and to be sure of its state of oxidization when weighed. Hence, if the sample contains much manganese, it is much better to dissolve the precipitate of oxide produced by the bromine, in a mixture of hydrochloric acid and sulphurous acid, and precipitate the manganese from this solution as manganese-ammonium phosphate, as previously directed. This method, to be sure, is much longer than the one just described, but it is also much more reliable, and, consequently, is to be recommended.

NATROLITE

33. Natrolite is a hydrous silicate of alumina and soda, but in addition to these constituents, most samples contain small quantities of iron and calcium. It is best to make a qualitative analysis of the sample before commencing a quantitative analysis, and if any of the constituents mentioned in the following scheme are not contained in the sample, the parts of the method that relate to those constituents should be omitted.

The sample is prepared for analysis by grinding a small portion to an extremely fine powder, drying it in an air bath at 100°, and cooling it in a desiccator. The constituents usually determined are: silica, alumina, ferric oxide, lime (calcium oxide), soda, and water.

34. Determination of Silica.—Weigh about 1.5 grams of the dry, finely powdered sample into a porcelain dish, add 50 cubic centimeters of concentrate hydrochloric acid, cover the dish with a watch glass, and digest on a water bath, with frequent stirring, until the sample is completely decomposed. Then remove the watch glass, wash any particles that may have spattered on it back into the dish with a fine jet of water, and evaporate the solution to dryness on the water bath. When perfectly dry, remove it to an air bath, and heat it to 110° for an hour, to render the silica insoluble. Moisten the residue with a few drops of concentrate hydrochloric acid, add from 100 to 150 cubic centimeters of hot water, and boil for a few minutes to dissolve the chlorides of the metals. Allow the precipitate to settle, filter, and wash thoroughly with hot water. Wrap the filter around the precipitate, place in a platinum crucible, ignite gently to burn the paper and expel water, and then heat for several minutes at the highest power of the blast lamp. Cool in a desiccator, and weigh as silica SiO_2.

35. Determination of Alumina.—The filtrate from the silica is heated to boiling in a beaker of rather deep form, which should hold at least twice the volume of the solution, and the aluminum is precipitated as hydrate, by slowly adding to the gently boiling solution, a very slight excess of pure ammonium hydrate, while stirring the solution continuously. Continue the boiling about 1 minute after the precipitation is complete, taking care that the solution remains faintly alkaline, and then stand it aside a few minutes, for the precipitate to subside. As soon as the precipitate has settled, filter, and wash the precipitate thoroughly with hot water. Fold the filter around the precipitate, place in a platinum crucible, and ignite, gently at first, to drive off moisture and burn the paper, but finally at the full power of the blast lamp. Cool in a desiccator, and weigh as alumina Al_2O_3.

If the sample contains iron, it will be weighed with the alumina, and after making a separate determination of iron

oxide, as directed in Art. **39,** the weight found must be subtracted from the alumina precipitate, in order to obtain the correct weight and percentage of alumina.

36. Determination of Calcium.—Evaporate the filtrate from the alumina to about 150 cubic centimeters, add 3 or 4 drops of concentrate ammonia, and then add ammonium oxalate in limited quantity and but slight excess. Continue the boiling for a minute or so after all of the reagent has been added, and then stand in a warm place for several hours till the precipitate has completely settled. Filter, and wash the precipitate thoroughly with hot water, receiving the filtrate and washings in a porcelain dish. Wrap the filter around the precipitate, place them in a platinum crucible, and ignite gently to drive off water and burn the filter. Then heat the crucible at the highest power of the blast lamp for 15 minutes, cool in a desiccator, and weigh. Ignite again for 5 minutes at the highest power of the blast lamp, cool in a desiccator, and weigh again. If this weight is less than the first one, the precipitate must be heated again at the highest power of the blast lamp, and this must be repeated until a constant weight is obtained. The precipitate now consists of lime CaO, and the percentage in the sample is calculated from this weight.

This method of determining the calcium oxide is probably the most satisfactory under ordinary circumstances if only occasional analyses are made. If preferred, however, the calcium-oxalate precipitate may be moistened with concentrate sulphuric acid, heated very gently until the calcium is converted into sulphate and the carbon dioxide expelled, then ignited more strongly over a Bunsen burner, cooled in a desiccator, and weighed as calcium sulphate $CaSO_4$, as directed under Determination of Calcium as Sulphate. Or, we may break the apex of the filter, then, with a mixture of sulphuric acid and water, wash the precipitate into a beaker, heat to about 75° and titrate with a standard solution of potassium permanganate, following the directions previously given.

37. Determination of Soda.—Evaporate the filtrate from the calcium oxalate to a small bulk in the porcelain dish, then transfer it to a platinum dish, washing the last portions of the solution in with a fine jet of distilled water, and evaporate to dryness. Place the dish in an air bath heated to about 100°, and gradually increase the temperature to about 150°. When all possibility of spurting is past, place the dish on a triangle, and cautiously heat it over a Bunsen burner until all ammonium salts are expelled, taking care to heat the dish to dull redness only, but making sure that every part of the dish is heated uniformly. When the ammonium salts are completely expelled, allow the dish to cool, and dissolve the residue of sodium chloride in a little water. Pour the solution through a small filter to remove any insoluble matter, and receive the filtrate in a weighed platinum dish, washing the sodium chloride out of the filter with the least necessary quantity of distilled water. Evaporate this filtrate to dryness, heat the dish to dull redness over the Bunsen burner after heating in the air bath to expel the last traces of water, cool in a desiccator, and weigh as sodium chloride $NaCl$. From this, calculate the percentage of soda Na_2O in the sample.

38. Determination of Water.—Grind a little of the sample to a coarse powder, dry it in an air bath at 100° and cool it in a desiccator. Weigh 2 or 3 grams of this coarse dry sample into a platinum crucible, and ignite carefully until a constant weight is obtained. The loss in weight is the weight of water, and from this, the percentage of water in the sample is calculated.

The crucible should be covered during ignition, and the sample used should be in the form of a coarse powder, as otherwise minute particles of the sample might be carried off with the water and thus yield erroneous results.

39. Determination of Iron.—If the qualitative examination has shown the presence of iron, this, of course, must be determined; and as the iron is precipitated in the

form of ferric oxide, with the alumina, the weight of ferric oxide found must be deducted from the weight of the alumina precipitate, before the percentage of alumina is calculated. Many chemists dissolve the alumina precipitate and determine the iron in this, but if this precipitate has been properly ignited, it is not entirely soluble in hydrochloric acid, and the writer prefers to determine the iron in a separate sample. Weigh from 1.5 to 3 grams of the dry, finely powdered sample into a porcelain dish, decompose it with concentrate hydrochloric acid in the same way that the original sample was decomposed, and evaporate to dryness. Moisten the residue with concentrate hydrochloric acid, add water, and heat to dissolve the chlorides of the metals. Filter off the silica, heat the filtrate to boiling, and precipitate the iron and alumina with a very slight excess of ammonia. Filter as soon as the precipitate settles, and wash once on the filter with hot water. Then remove as much as possible of the precipitate from the filter to a beaker or porcelain dish, stand this under the funnel, and dissolve the small quantity of precipitate adhering to the filter in a little hot, dilute hydrochloric acid, allowing this solution to run into the vessel containing the precipitate. Add a few more drops of hydrochloric acid to the filter, and wash all iron out of it with the least necessary quantity of water. Heat the vessel containing the precipitate and acid solution until the precipitate is dissolved, adding a little concentrate hydrochloric acid, if necessary. Wash this solution into a flask, reduce it with zinc, add sulphuric acid, and titrate with permanganate, following the directions previously given.

From the weight of iron obtained by titration, calculate the weight and percentage of ferric oxide Fe_2O_3 in the sample. If the weight of the sample taken for the analysis is the same as the weight of sample taken for the determination of iron, the correction for alumina may be made by subtracting the weight of ferric oxide found, from the weight of the alumina precipitate. If different weights of sample are taken, the weight of ferric oxide in the alumina precipitate

must be calculated, by means of a proportion, or the percentage of ferric oxide found must be subtracted from the percentage of alumina and iron.

PREHNITE.

40. Prehnite is essentially a hydrous silicate of aluminum and calcium, but in addition to these constituents, most samples contain varying quantities of iron, manganese, and the alkalies. To prepare the sample for analysis, grind it to an exceedingly fine powder in a mortar, heat to 100° for 1 hour in an air bath, and cool in a desiccator.

Before commencing a quantitative analysis of the sample, it should be subjected to a qualitative examination, and if any of the constituents mentioned in the following method are not contained in it, those parts relating to such constituents should be omitted.

41. Determination of Silica.—Into a porcelain dish weigh about 1.5 grams of the dry, finely powdered sample, add 50 cubic centimeters of concentrate hydrochloric acid, cover the dish with a watch glass, and digest on the water bath till decomposition is complete, stirring the sample from time to time during this treatment. When decomposition is complete, remove the watch glass, wash back into the dish any particles that may have spattered on it during the decomposition, and evaporate the solution to complete dryness on the water bath. Heat the residue on the sand bath or in an air bath to render the silica insoluble, but take care not to heat it sufficiently to cause recombination of the silica and alumina. Moisten the residue with concentrate hydrochloric acid, add from 100 to 150 cubic centimeters of water, and heat gradually to boiling to dissolve the chlorides of the metals, leaving the silica as a precipitate. Filter, and wash the precipitate thoroughly with hot water. Wrap the filter around the precipitate, place them in a platinum crucible, ignite gently at first to drive off the water, and burn the paper, then raise the temperature and ignite at the full

power of the blast lamp for a few minutes. Cool in a desiccator, and weigh as silica SiO_2.

42. Determination of Alumina.—The filtrate from the silica is heated to boiling, in a beaker of rather deep form which should hold about twice the volume of the solution, and the alumina is precipitated by slowly adding ammonium hydrate—which must be free from carbon dioxide—to the gently boiling solution, while stirring continuously. Continue the boiling for a minute or so after precipitation is complete, taking care that the solution remains faintly alkaline. Then stand the beaker and contents aside for a few minutes for the precipitate to subside. As soon as the precipitate has settled, filter, wash once or twice with hot water, and stand the filtrate aside. The precipitate now contains all the alumina and iron—if there was any iron in the sample—together with part of the calcium, and probably some of the alkalies. These latter elements must be separated by reprecipitation. To do this, dissolve the precipitate in a small quantity of hydrochloric acid, dilute the solution to about 150 cubic centimeters, heat to boiling, and precipitate the alumina with a slight excess of pure ammonium hydrate in the same manner that the first precipitation was made. Filter, as soon as the precipitate settles, and wash thoroughly with hot water. Wrap the paper around the precipitate, place them in a platinum crucible, and, after heating gently to expel moisture and burn the paper, ignite for several minutes at the full power of the blast lamp. Cool in a desiccator, and weigh as alumina Al_2O_3.

If the sample contains iron, it will be precipitated and weighed with the alumina in the form of ferric oxide Fe_2O_3, and a correction must be made. The iron is determined as previously directed, calculated to ferric oxide, and reported as such. The ferric oxide thus found is subtracted from the alumina precipitate, which also contains the iron, and the difference is pure alumina.

43. Determination of Manganous Oxide.—Unite the filtrates from the first and the second precipitation of alumina,

and evaporate to about 100 cubic centimeters. Pour this solution into a flask that it will almost fill, add a few drops of ammonium sulphide, stopper the flask, and stand it in a warm place for 24 hours for the precipitate of manganese sulphide MnS to collect and settle. Filter, and wash as rapidly as possible with water containing a very little ammonium sulphide. Excessive washing should be avoided.

Remove the filter containing the precipitate from the funnel to a beaker, add hydrochloric acid, and heat the mixture till the odor of hydrogen sulphide is no longer given off. Dilute the acid mixture with two or three times its volume of water, filter, and wash the residuary filter paper carefully, receiving the filtrate in a porcelain dish. Heat the filtrate to boiling; then remove the burner, and slowly add a solution of sodium carbonate, while stirring continuously, until the solution has a strong alkaline reaction. Boil a few minutes to expel carbon dioxide, allow the precipitate to settle, filter, and wash the precipitate with hot water until the washings are no longer alkaline to litmus paper. Dry the precipitate, remove it as completely as possible from the filter, and burn the latter in a weighed platinum crucible. When cool, add the precipitate, and heat over the blast lamp for 10 or 15 minutes, leaving the cover off of the crucible to freely admit the air, but taking care to avoid the action of reducing gases. Cool in a desiccator and weigh. The precipitate is now manganous-manganic oxide Mn_3O_4, and from this, the weight and percentage of manganous oxide MnO are readily calculated.

44. Determination of Calcium Oxide.—In order to determine the calcium that is present in the mineral, acidify the filtrate, obtained from the precipitation of the manganese as manganese sulphide, with hydrochloric acid, evaporate to 150 or 200 cubic centimeters, add an excess of ammonium hydrate, and then slowly add to the gently boiling solution a slight excess of ammonium oxalate and a few more drops of ammonia. Continue the boiling for a few minutes and then stand in a warm place for 3 or 4 hours.

Filter, wash the precipitate once or twice with hot water, and stand the filtrate aside. As prehnite contains a large percentage of calcium, a portion of the alkalies will frequently be carried down with this precipitate, and must be separated from it by reprecipitation. Dissolve the precipitate in the least necessary quantity of hydrochloric acid, dilute the solution to about 150 cubic centimeters, and heat it to boiling. To the gently boiling solution, slowly add ammonium hydrate in very slight excess; then add a few drops of ammonium-oxalate solution and boil for a minute or two. After allowing the solution to stand in a warm place 3 or 4 hours for the precipitate to collect and settle, filter, and wash thoroughly with hot water. Wrap the filter around the precipitate, place them in a platinum crucible, and after heating gently to drive off water and burn the paper, ignite at the highest temperature of the blast lamp for 15 or 20 minutes, cool in a desiccator, and weigh quickly. Then ignite again for 5 minutes at the highest power of the blast lamp, cool, and weigh. If this weight varies appreciably from the first weight, the ignition must be continued until a constant weight is obtained, when the precipitate will be calcium oxide CaO.

If preferred, the calcium-oxalate precipitate may be converted into sulphate (see Determination of Calcium as Sulphate), or the calcium oxide may be determined volumetrically, by means of potassium permanganate, as previously directed.

45. Determination of Potassium Oxide.—Acidify the united filtrates from the calcium oxalate with hydrochloric acid, boil, and filter to remove any precipitate that may have separated. Then evaporate the solution to dryness in a platinum dish, heat to about 150° in an air bath, and finally heat to dull redness over a Bunsen burner to expel ammonium salts, following the directions given in Art. **37.** Dissolve the residue in a little distilled water, and filter into a weighed platinum dish. Evaporate this solution to dryness, heat it in an air bath to about 150°, and finally heat it to dull redness over a Bunsen burner, taking care to heat

every part of the dish uniformly. Cool in a desiccator, and weigh quickly as soon as cool. The residue now consists of the chlorides of sodium and potassium.

Dissolve the residue of mixed chlorides in the least necessary quantity of cold water, add a strong solution of platinic chloride in sufficient quantity to convert all of the potassium and sodium into the double chlorides of these metals and platinum, and evaporate to a pasty consistence over a water bath in which the water is held as near the boiling point as possible. To the pasty mass in the platinum dish, add 35 or 40 cubic centimeters of 80-per-cent. alcohol, cover it with a watch glass, and stand it in a warm place for an hour or two, stirring from time to time. Decant the liquid through a weighed filter, wash once by decantation with 80-per-cent. alcohol, then transfer the precipitate to the filter, and wash thoroughly, but not excessively, with alcohol of the same strength. Dry the precipitate in an air bath at 130° for at least an hour, and longer if necessary. Weigh as potassium-platinic chloride K_2PtCl_6, and from this weight, calculate the weight and percentage of potassium oxide K_2O in the sample.

46. Determination of Sodium Oxide.—As sodium cannot be determined by precipitating and weighing it, when it is separated from potassium gravimetrically, it is always determined by difference. This is done as follows: From the weight of potassium-platinic chloride obtained, calculate the weight of potassium chloride KCl, and subtract this from the weight of the mixed chlorides of sodium and potassium previously obtained. The remainder would obviously be the weight of sodium chloride $NaCl$, and from this, the weight and percentage of sodium oxide Na_2O in the sample is readily calculated.

Instead of using the gravimetric method just described to separate sodium and potassium, the volumetric method described under Separation of Potassium and Sodium, may be employed for this purpose.

47. Determination of Water.—If the sample is free from organic matter, the water of constitution may be

determined by weighing a convenient quantity of the dry sample in a crucible, igniting, and weighing again, when the loss will represent the water of constitution. But as many samples of prehnite contain organic matter, another method for the determination of water must frequently be employed. When organic matter is present, which is indicated by the sample becoming dark colored when heated, the following method is recommended. Take a piece of combustion tubing about 3 feet long, having an internal diameter of about $\frac{1}{2}$ inch, heat it in the center by means of a blast lamp until it softens, draw the ends apart slightly, and then, keeping the two parts of the tube parallel, draw it out as shown in Fig. 1.

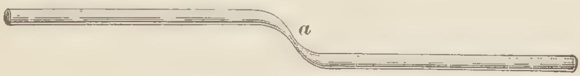

FIG. 1

When cool, scratch the tube at the point *a* with a file, and break it off. Two tubes, each about 18 inches in length, are thus obtained. Heat the small end of one of these tubes in a blast-lamp flame until it fuses shut. By means of a glass rod push a little ignited asbestos loosely into the closed end of the tube, but do not pack it in tight. Then add enough pure powdered lead chromate to fill the tube for about 1 inch of its length. Next weigh out 1 gram of the dry, powdered sample, mix it intimately with 15 grams of fused and powdered lead chromate, and 1.5 grams of fused and powdered potassium bichromate, and introduce this mixture into the tube. Clean out the vessel (usually a mortar) in which these substances were mixed, by grinding two or three small portions of lead chromate in it, and charge these into the tube. Now lay the tube in a horizontal position, and, while holding the closed end up, rap it gently on the table to get a clear space along the top of the tube, for the free passage of gas or vapors, from one end of the tube to the other. Fit the open end of the tube with a singly perforated rubber stopper, and through the perforation pass one end of a **U** tube which is filled with dry calcium chloride and weighed. The tube will now appear as shown

in Fig. 2. Place the tube in a combustion furnace (which is described in *Organic Chemistry*) and gradually turn on the burners, beginning at the closed end of the tube, *a*, Fig. 2. After the tube has been heated to redness throughout its entire length, turn out the burners next to the end *a*, and when

FIG. 2

this has partially cooled, slip a piece of rubber tubing over the end *a* of the combustion tubing that was drawn out and sealed. Attach a drying tube filled with calcium chloride to the other end of the rubber tube, and then by means of a pair of pincers, break the tip *a* of the combustion tube, inside of the rubber tube. By means of a piece of rubber tubing slipped over *b*, attach the **U** tube to an aspirator, and draw about 1 liter of air through the apparatus. Turn out the lights, disconnect the apparatus, and weigh the **U** tube. The increase in weight is the weight of water in the sample.

Instead of using lead chromate and potassium bichromate, some chemists prefer gently ignited lead carbonate. The writer prefers the method as given above.

WOLFRAMITE

48. Wolframite is a tungstate of iron and manganese, containing these metals in varying proportions. Its composition may be expressed by the formula $(FeMn)WO_4$, but in addition to these elements it frequently contains small quantities of calcium and magnesium. The mineral is very difficult to dissolve in acids, and, consequently, it is best to fuse it with alkaline carbonates in order to decompose it. The sample is prepared for analysis by grinding it to a powder in an agate mortar, heating it in an air bath at

about 110° to drive off any moisture, and cooling it in a desiccator.

49. Determination of Tungstic Oxide.—Weigh out 1 gram of the dry, finely powdered sample, mix it intimately with four times its weight of mixed carbonates (a mixture of equal parts of sodium and potassium carbonates) and introduce the mixture into a platinum crucible. Heat the crucible over a blast lamp until the contents are in a state of quiet fusion. Allow the crucible and contents to cool, and extract the fusion with hot water. Filter, and wash thoroughly with hot water. The tungsten will now be in the filtrate in the form of soluble sodium tungstate, while the insoluble residue contains the iron, manganese, calcium, and magnesium.

The tungsten may be separated from the filtrate in the form of tungstic acid or of mercurous tungstate. The second method is probably the one most generally used.

1. *Separation as Tungstic Acid.*—Render the filtrate acid with hydrochloric acid, evaporate to dryness on a water bath, and heat the residue to about 120° in an air bath for some time. Dissolve the alkaline chlorides in water and hydrochloric acid, filter, and wash the tungstic acid thoroughly on the filter with water containing hydrochloric acid. Wash the moist precipitate with hot ammonia, and catch this filtrate, which will contain the tungstic acid, in a separate vessel. Evaporate to a small bulk, transfer to a weighed platinum crucible, evaporate to dryness, ignite, allow the crucible to cool, moisten the WO_3 with nitric acid, again dry, and ignite strongly. Cool in a desiccator, and weigh as tungstic oxide WO_3. A constant weight must be obtained, and the precipitate should have a pure yellow color. If its color is not yellow, it should be moistened with a few drops of pure nitric acid, and again ignited with free access of air, cooled in a desiccator, and weighed.

2. *Separation of Mercurous Tungstate.*—To the alkaline filtrate, add a slight excess of nitric acid, so that, after driving out the carbon dioxide by heat, the solution has a

slight acid reaction. Stand this solution in a moderately warm place for 24 hours, and then add a solution of mercurous nitrate, and a little mercuric oxide HgO suspended in water. Allow the precipitate to completely subside, collect it on a filter, and wash it well with water containing mercurous nitrate. Dry the precipitate in an air bath, remove it as completely as possible from the filter, moisten the latter with a strong solution of ammonium nitrate, and burn it carefully in a weighed crucible. When the crucible becomes cool, add the precipitate and carefully ignite it with free access of air, under a hood or chimney with a strong draft. Cool in a desiccator and weigh as tungstic oxide WO_3. The ignition should be repeated until a constant weight is obtained. When this method is used, the precipitate should be ignited under a hood having a strong enough draft to carry off the mercury vapors.

50. Determination of Iron.—Dissolve the precipitate containing the iron and manganese—as well as calcium and magnesium if these were contained in the mineral—in hydrochloric acid. Heat the solution to boiling, add a few drops of concentrate nitric acid, and continue the boiling until the solution assumes a clear yellow color, showing that the iron is completely oxidized to the ferric state. When the solution becomes cold, dilute it moderately with cold water, and while stirring continuously, slowly add a solution of sodium carbonate until the solution assumes a deep reddish-brown color, but stop the addition before a permanent precipitate forms. If, by mistake, too much sodium carbonate is added, so that a precipitate that is not dissolved by stirring the cold solution for a minute or two is formed, add a drop or two of hydrochloric acid and stir until it dissolves, but keep the solution as near the neutral point as possible. To this cold solution, add a slight excess of sodium acetate and heat it to boiling for a few minutes. The iron will be precipitated as basic ferric acetate together with more or less manganese, depending largely upon the amount of sodium acetate added in excess of the amount required to

precipitate the iron. Probably 5 cubic centimeters of a cold saturated solution of sodium acetate will always be sufficient for this purpose, and the smaller the quantity added in excess of the required amount, the better.

Wash the precipitate three or four times in hot water, stand the filtrate aside, and dissolve the precipitate in hot, dilute hydrochloric acid. Dilute this solution moderately with cold water, and when cold, neutralize it with sodium carbonate, add sodium acetate, and precipitate by boiling as in the first instance. The precipitate should now contain only the iron, in the form of basic acetate. Filter as soon as the precipitate settles, and wash thoroughly on the filter with hot water. Wrap the filter around the precipitate, place them together in a platinum crucible, heat gently to drive off water and burn the paper, and then ignite strongly over the blast lamp. Cool the crucible and precipitate in a desiccator, and weigh as ferric oxide Fe_2O_3. From this weight, calculate the weight and percentage of ferrous oxide FeO in the sample.

51. Determination of Manganese.—Unite the filtrates from the two acetate precipitations of the iron, and if the bulk of the combined filtrates greatly exceeds 200 cubic centimeters, it should be concentrated to 150 or 200 cubic centimeters before proceeding. To this solution, add about 10 cubic centimeters of a saturated solution of sodium acetate, heat it nearly to boiling, and add pure bromine until the solution has a strong yellow color. Three or four cubic centimeters will be about the right amount. Heat the solution on the water bath for an hour, and if the clear liquid loses its yellow color during this time, add more bromine. Then boil the solution over a Bunsen burner to expel the excess of bromine, and stand it on a water bath for the precipitate of hydrated manganese dioxide to settle. Filter, and wash thoroughly with hot water, taking care not to stir up the precipitate, or it may run through the paper. When thoroughly washed, dissolve the precipitate in a mixture of sulphurous and dilute hydrochloric acids, receiving the solution in a clean beaker. When all is dissolved, wash the filter

thoroughly. Boil the solution to expel the sulphur dioxide, precipitate the manganese as manganese ammonium phosphate, by means of microcosmic salt, and after ignition, weigh it as manganese pyrophosphate, following the directions given in Art. **22.** From the weight of manganese pyrophosphate $Mn_2P_2O_7$ thus obtained, calculate the weight and percentage of manganous oxide MnO in the sample.

If the sample is a pure ferrous manganous tungstate, this will complete the analysis, but as most samples contain more or less calcium and magnesium, the analysis must generally be extended to include these elements.

52. Determination of Calcium.—To the filtrate from the manganese-dioxide precipitate, add ammonia until it is strongly alkaline, heat to boiling, and add a moderate excess of ammonium oxalate to precipitate the calcium. Continue the boiling for a few moments, and then stand the solution in a moderately warm place for 3 or 4 hours for the precipitate to collect and settle, taking care that the solution remains distinctly alkaline. Filter, and wash thoroughly with hot water containing a little ammonia. Wrap the filter around the precipitate, place them in a platinum crucible, and after heating gently to drive off moisture and burn the paper, ignite for 15 or 20 minutes at the highest power of the blast lamp. Cool in a desiccator, and weigh as calcium oxide CaO.

53. Determination of Magnesium.—Evaporate the filtrate from the calcium oxalate to a small bulk, cool it by standing the beaker in ice water, and precipitate the magnesium as magnesium-ammonium phosphate, by slowly adding a solution of microcosmic salt, while stirring the solution continuously. Add to the solution about one-fourth its volume of ammonium hydrate, stir it vigorously two or three times without allowing the stirring rod to touch the side or bottom of the beaker, and then stand it in a cold place for at least 6 hours for the precipitate of magnesium-ammonium phosphate to collect and settle. Filter, and wash the precipitate with water containing one-fourth its volume of ammonia. Dry it

in an air bath, remove the precipitate as completely as possible from the filter, and burn the latter in a weighed crucible. When cool, add the precipitate, ignite intensely over a blast lamp, cool in a desiccator, and weigh as magnesium pyrophosphate $Mg_2P_2O_7$. From this weight, calculate the weight and percentage of magnesium oxide MgO in the sample.

FELDSPAR

54. Feldspar is a silicate of aluminum, potassium, and sodium, and usually contains smaller quantities of the oxides of iron, calcium, and magnesium. It is not decomposed by acids, and consequently must be fused. This necessitates working on two samples, for the alkalies cannot be determined in the portion fused with sodium and potassium carbonates for the determination of the other elements, and the other constituents cannot be determined accurately in the portion treated for the alkalies.

As a number of other substances have much the same composition as feldspar, the method here given may be used in a number of instances by modifying it slightly to suit each particular case. For instance, ordinary mica contains the same constituents as feldspar, but in somewhat different proportions; and the same may be said of sandstone and ordinary glass, except that these may also contain manganese oxide. This statement cannot be made to include all varieties of glass, however, for different varieties vary in their composition. For instance, flint glass contains considerable lead, and but little calcium, lead oxide being substituted for calcium oxide in this variety.

Great care must be taken in the preparation of a sample of feldspar for analysis, for the mineral is very difficult to decompose. It should be ground in an agate mortar, in small portions at a time, until it is so fine that no gritty particles can be felt with the pestle. This powder is then dried in an air bath for an hour at about 110° and cooled in a desiccator.

55. Determination of Silica.—Mix 1 gram of the dry, powdered sample with about 6 grams of mixed carbonates (equal parts of sodium and potassium carbonates) in an agate mortar, and introduce this mixture into a 50-gram platinum crucible. Rinse out the mortar with about 2 grams of the mixed carbonates and pour this on top of the mixture in the crucible. Cover the crucible, and heat gently over a Bunsen burner at first, then gradually raise the temperature to the full power of the blast lamp, and maintain this heat till the contents of the crucible have been in a state of quiet fusion for some time. Turn out the gas, and cool quickly by at once standing the crucible on a large clean plate of cold metal. The hot crucible is usually handled by means of the crucible tongs shown in Fig. 3. When partly cooled,

FIG. 3

the crucible may be dipped into ice water, but care must be taken not to allow any water to get inside of the crucible. When cooled quickly in this way, the fusion may generally be removed from the crucible without difficulty, as soon as cold.

Invert the crucible in a porcelain dish, and tap it gently, when the fusion will usually fall out in the dish. Leave the fusion and crucible both in the dish, add about 75 cubic centimeters of water and heat to boiling. Then cover the dish with a watch glass and slowly add hydrochloric acid until the liquid has a strong acid reaction and the fusion is dissolved. Remove the crucible from the dish and wash it off by means of the wash bottle, allowing the washings to run into the dish. Wash the watch glass off into the dish, and then evaporate the solution to dryness on the water bath, stirring frequently towards the last. When quite dry, pulverize the residue with a small agate pestle, and brush any of the residue that may adhere to the pestle back into

the dish by means of a camel's-hair brush. Then place the dish and contents in an air bath and heat it at 120° to 125° for 2 hours, to render the silica insoluble. After the residue has become cool, add 30 cubic centimeters of concentrate hydrochloric acid, and digest it on a water bath for about half an hour. Then add 100 cubic centimeters of water, and heat to boiling for 10 or 15 minutes over a Bunsen burner to dissolve the chlorides of the metals. Filter, and wash thoroughly with hot water. The washing should be continued until the wash water comes through the filter free from hydrochloric acid. Suck the precipitate and filter as dry as possible by means of the filter pump, wrap the filter around the precipitate, place them in a platinum crucible, and, after heating gently to drive off water and burn the paper, ignite at the full power of the blast lamp. Cool in a desiccator, and weigh as silica SiO_2.

56. Determination of Iron and Alumina.—Concentrate the filtrate from the silica to 150 or 200 cubic centimeters, heat it to boiling, and precipitate the iron and alumina by adding a very slight excess of ammonia to the gently boiling liquid, while stirring it continuously. Continue the boiling for a few moments, but be sure that a faint odor of ammonia can still be observed. Filter as soon as the precipitate settles, preferably while the liquid is still warm, and wash thoroughly with hot water. Suck the precipitate and filter as dry as possible by means of the pump, wrap the filter around the precipitate, place them in a platinum crucible, and after driving off moisture and burning the paper at a gentle heat over the Bunsen burner, ignite intensely over the blast lamp. Cool in a desiccator, and weigh as the oxides of aluminum and iron $Al_2O_3 + Fe_2O_3$.

Fuse the precipitate with about eight times its weight of acid potassium sulphate, heating the fusion until the second molecule of sulphuric acid is expelled, leaving the normal sulphate. When cool, add a volume of pure, concentrate sulphuric acid, equal to that of the fused mass, and heat cautiously until the contents of the crucible become fluid.

When cool, place the crucible in a porcelain dish containing hot water, and digest over a low flame until the contents of the crucible are completely dissolved. Transfer the solution to a flask, add about 15 cubic centimeters of pure, dilute sulphuric acid and 10 grams of granulated zinc, place a small funnel in the mouth of the flask and stand in a moderately warm place until the iron is reduced. Filter the solution through a large folded filter, wash this by filling it with cold water and allowing it to run through into the main solution, and titrate at once with potassium permanganate.

It is necessary in this case to make a blank determination to ascertain the amount of permanganate consumed by substances other than the iron in the sample. This is done as follows:

In a clean platinum crucible place the same weights of acid potassium sulphate and sulphuric acid as were used in fusing the precipitate of iron and alumina, and cautiously heat until the bisulphate is dissolved. After allowing this to cool, take it up in water, transfer the solution to a flask, add the same amounts of zinc and sulphuric acid as were used in the regular determination, place a small funnel in the mouth of the flask, and allow this solution to stand the same length of time as the main solution. Filter, wash the filter paper, and titrate with potassium permanganate. Deduct the volume of permanganate consumed by the blank from the amount used in the regular determination; the remainder is the amount used in oxidizing the iron in the sample. From this, calculate the weight and percentage of ferric oxide Fe_2O_3 in the sample. The weight of Fe_2O_3 thus obtained, subtracted from the weight of $Al_2O_3+Fe_2O_3$, gives the weight of aluminum oxide Al_2O_3 in the sample, and from this, the percentage is calculated.

Instead of fusing the precipitate of iron and alumina with acid potassium sulphate in order to determine the iron, some chemists prefer to fuse a fresh portion of the original sample with mixed carbonates, filter off the silica, precipitate the iron and alumina as in the regular analysis, dissolve this precipitate in the least necessary quantity of hydrochloric

acid, reduce the iron, and titrate with permanganate, following the directions previously given.

57. Determination of Calcium.—If the filtrate from the iron and alumina exceeds about 200 cubic centimeters, as will usually be the case, evaporate it to about this bulk. Then to the boiling solution, add a moderate excess of ammonium oxalate and 10 or 15 cubic centimeters of ammonium hydrate, and continue the boiling for a few minutes, stirring continuously to prevent bumping. Stand the solution in a warm place for at least 4 hours for the precipitate of calcium oxalate to separate. Filter and wash thoroughly with hot water containing a little ammonia. Suck the precipitate and filter as dry as possible by means of the filter pump, wrap the filter around the precipitate, place them in a platinum crucible, and after heating gently to expel moisture and burn off the paper, ignite for 15 or 20 minutes at the full power of the blast lamp. Cool in a desiccator, and as soon as cool, weigh quickly. Then reignite for 5 minutes at the highest temperature of the blast lamp, cool in a desiccator, and weigh. This must be repeated until a constant weight is obtained, when the precipitate will be calcium oxide CaO.

58. Determination of Magnesium.—Evaporate the filtrate from the calcium to 150 or 200 cubic centimeters, and cool it by standing the beaker containing it in ice water. When cold, add a moderate excess of microcosmic-salt solution $HNaNH_4PO_4$ and 35 or 40 cubic centimeters of ammonia. Stir the solution vigorously for some time, taking care not to let the stirring rod strike the side of the beaker, and then stand it aside in a cool place for at least 6 hours for the precipitate of magnesium-ammonium phosphate to form and settle. Filter, and wash the precipitate thoroughly with a mixture of 1 part of ammonia and 3 parts of water, containing 50 grams of ammonium nitrate to the liter. Dry the precipitate, remove it as completely as possible from the filter, and cautiously burn the latter in a porcelain

crucible. When cool, add the precipitate, and ignite at a gradually increasing temperature, finally heating strongly over the blast lamp. Cool the precipitate in a desiccator and weigh as magnesium pyrophosphate $Mg_2P_2O_7$. From this weight, calculate the weight and percentage of magnesium oxide MgO in the sample.

59. Determination of Alkalies.—The best method for the determination of the alkalies in insoluble silicates, and the one generally employed, was proposed by Dr. J. Lawrence Smith. Dr. Smith devised an excellent crucible and burner for this purpose, but as the cost of this apparatus is considerable, an ordinary platinum fusion crucible is frequently employed in its stead, and serves the purpose very well.

Accurately weigh .5 gram of the finely pulverized sample into a large agate or glazed porcelain mortar, add an equal weight of pure ammonium chloride, and grind the two together intimately. Then to the contents of the mortar, add a weight of pure calcium carbonate equal to eight times the weight of the sample, in three or four successive quantities, mixing intimately after each addition. During the mixing the mortar should stand on a piece of glazed paper to catch any particles that may fly out. When thoroughly mixed, pour the contents of the mortar on the glazed paper, and from this transfer it to the platinum crucible. Rinse out the mortar by grinding a little more calcium carbonate in it, pour this on the glazed paper, and from the paper transfer it to the crucible, thus making sure of getting all the sample in the crucible. Tap the crucible gently on the table to settle the contents down, cover it, and place it on the triangle in a slanting position, be sure that the crucible should remain closely covered. Bring a Bunsen burner with the flame turned low under the crucible, so that the flame strikes about the top of the mixture, and heat it to faint redness. Turn the crucible from time to time so that each part is equally heated, and gradually move the burner toward the bottom of the crucible.

When fumes of ammonium chloride are no longer given off, turn the flame higher, and heat for an hour, turning the crucible and moving the burner from time to time to be sure that all parts of the mixture are subjected to the same temperature. Too intense an ignition should be avoided, as it is likely to vitrify the mass too much. A dull-red heat is sufficient. After allowing the crucible to cool, the contents will be found agglomerated in a semifused mass, which may be removed by tapping the crucible.

By inverting the crucible in a porcelain dish and gently tapping it, or by cautiously using a stirring rod, if necessary, remove the mass to the porcelain dish. Wash any particles that may adhere to the crucible into the dish with hot distilled water, wash off the crucible lid in the same way, and then continue the addition of distilled water until about 80 cubic centimeters have been added. Cover the dish with a watch glass, and heat the contents to boiling over a Bunsen burner. The mass will usually slake and crumble like lime in a few minutes. If it should not, cautiously grind it up in the dish by means of an agate pestle, and digest it on a water bath until it is completely slaked.

If the mass should be hard to detach from the crucible, do not use much force in trying to remove it, or the crucible may be injured, but fill the crucible to about two-thirds its capacity with water, heat it nearly to boiling, and let it stand a short time, when the mass will slake and may be washed out.

Filter, and wash the precipitate until a few drops of the washings, acidified with nitric acid, give only a slight cloudiness when treated with silver nitrate. About 200 cubic centimeters of water will be required for this washing. The filtrate now contains the potassium and sodium in the form of chlorides, together with ammonium chloride and some calcium chloride formed in the operation. All that remains is to separate the calcium as carbonate, and volatilize the ammonium chloride, in order to obtain the chlorides of sodium and potassium free from other elements. This is done as follows:

Dissolve about 1.5 grams of pure ammonium carbonate in water, and add this to the filtrate, thus precipitating all the calcium as carbonate. Do not filter at once, but place the solution containing the precipitate on a water bath, and evaporate it to about 50 cubic centimeters. Then add a little more pure ammonium carbonate and a few drops of ammonium hydrate, to reprecipitate any calcium dissolved by the action of the ammonium chloride on the calcium carbonate. Bring the solution just to boiling, filter through a small filter, and wash the precipitate with the least necessary quantity of water. Add a few drops of ammonium carbonate and a drop or two of ammonium hydrate to the filtrate, and, if a precipitate forms, filter it off. Evaporate the solution to dryness on a water bath, preferably in a platinum dish; dissolve the residue in the least necessary quantity of water, and add a few drops of ammonium carbonate and a drop or two of ammonium hydrate to precipitate any calcium that may thus far have escaped precipitation. Filter, and wash with a small volume of water, receiving the filtrate in a weighed platinum dish. Evaporate to dryness on a water bath, then place the dish in an air bath heated to 100°, and gradually raise the temperature to 150° to expel all the water and avoid danger of spattering when more strongly heated. Place the dish on a triangle, and heat it over a Bunsen burner, moving the burner from place to place in order to heat each part of the dish equally. Heat the dish to faint redness until the ammonium chloride is completely expelled, but avoid a higher temperature, lest some of the sodium and potassium chlorides be volatilized. When ammonium salts are completely driven off, cool in a desiccator, and weigh as $KCl + NaCl$. Dissolve the residue in the least necessary quantity of water, precipitate the potassium as potassium-platinic chloride, and from the weight of this obtained, calculate the weight and percentage of potassium oxide K_2O in the sample. Then, from the weight of potassium-platinic chloride, calculate the weight of potassium chloride, and by subtracting this weight from the weight of the mixed chlorides, obtain the weight of sodium chloride. From this,

calculate the weight and percentage of sodium oxide Na_2O in the sample, following the directions given for the separation of the alkalies in Arts. **45** and **46.**

60. Loss on Ignition.—Although feldspar does not normally contain water of constitution, many samples dried at 110° lose weight when subjected to a higher temperature. This loss in weight is sometimes reported as water, but as it may be due to other things, and as the loss is not great enough to be of sufficient importance to justify an examination as to its cause in each case, it has become customary to report it as *loss on ignition.* The determination is made as follows:

Weigh into a platinum crucible 2 or 3 grams of the pulverized sample, which has been dried at 110°, heat it over a Bunsen burner for 20 minutes, cool in a desiccator, and weigh again. From the loss in weight, calculate the percentage of loss.

The sample used for this determination does not need to be as finely powdered as those used for the fusions. In fact, it is best to have this sample a little coarser, as there is then less danger of particles of it being carried out of the crucible by the draft during ignition.

QUANTITATIVE ANALYSIS

(PART 5)

IRON ANALYSIS

GENERAL REMARKS

1. Thus far the work in quantitative analysis has been confined to the determination of single elements in chemical compounds of known composition, and to the complete analysis of substances, in both of which cases a student could check his work: in the first instance, by calculating the theoretical percentage of the element sought, in the compound analyzed; and in the second, by adding together the percentages of the different constituents found, to see how near the sum of the constituents approaches 100 per cent.

In *Quantitative Analysis*, Parts 1 and 2, we endeavored to describe the most approved methods of determining the principal elements in a way that would give the student a good general idea of the methods of quantitative work, and, at the same time, some experience in the determination of the elements most frequently met. In Parts 3 and 4, the knowledge obtained in Parts 1 and 2 is put in practice in the analysis of a few typical compounds, alloys, and minerals, chosen with a view to rendering the student familiar with the general methods of analysis.

In a work of this character it would be impossible to

describe the analysis of every existing compound, alloy, and mineral, and no attempt has been made to do so. Instead of this, we have attempted, by means of a few typical examples, to render the student so familiar with the different processes that he can readily apply his knowledge in all similar cases; and, if he has worked faithfully on his papers up to this point, he should now be able to analyze any compound, alloy, or mineral likely to be met.

The following work, which deals with technical analysis, is built up largely on the same principles as the preceding, but differs from it in several respects. As a rule, a complete analysis is not required, but merely the determination of some of the constituents, generally those on the percentage of which the value or quality of the substance depends. Hence, in much of the succeeding work the accuracy of the results cannot be determined by the methods previously employed, and, except in the case of determinations that are made daily, the results should always be checked by making duplicate determinations. In the laboratories of manufacturing establishments where a chemist determines the same elements in many samples every day, it would generally be impossible to make duplicate determinations in each case, and it is hardly necessary, for he soon becomes so familiar with his routine work that he is not likely to make a mistake; but even in these cases, it is a good plan to make duplicate determinations if time permits, and any determination outside of the regular work should always be checked by a duplicate.

So many methods are employed in iron and steel works chemistry at the present time that it would be impossible to describe them all in this Paper. Consequently, only one or two methods, as a rule, will be given for the determination of each element. In the case of elements for the determination of which several methods are largely employed, one strictly accurate method and one or two of the more rapid methods will generally be described. In experienced hands most of these short or rapid methods will yield extremely accurate results with most samples, and, on account of their

rapidity—enabling a chemist to do a great deal of work and to obtain results in a short time—they are used almost exclusively in iron and steel works laboratories. As some of them do not give accurate results in all cases, it is necessary for the iron-works chemist to be familiar with longer methods that will yield exact results in every case, and, for this reason, both short and long methods are described.

IRON ORES

2. As iron ore is the principal "raw material" in the manufacture of iron, its analysis will be treated first. This is an important matter, for the value of the ore depends on its composition Other things being the same, the value of an ore depends on the amount of iron it contains, but the percentage of iron is not the only consideration, for other constituents have much to do with fixing its value for certain uses. Thus, an ore containing much phosphorus, however rich in iron it may be, would be unsuited for the production of pig iron to be used in the manufacture of Bessemer steel, because the phosphorus in the ore would pass into the steel and render it unfit for use.

An analysis is not only useful in determining the value of an ore, but also to determine the quantity of other material that is to be charged into the furnace with it. Thus, the amount of limestone added to form a slag with impurities depends on the amount of impurity to be "slagged off." The principal determinations in the analysis of iron ores are *insoluble matter* and *silica*, *iron*, *phosphorus*, *sulphur*, *manganese*, and sometimes *water*.

3. Selection and Preparation of a Sample.—The selection of a sample is a matter of importance, for, if the results of the analysis are to be of any value, a sample must be chosen that accurately represents the whole quantity of which the analysis is supposed to show the composition.

In order to obtain such a sample, the following points

should be observed: the relative amount of fine ore and lumps in the lot to be sampled should be carefully noted, and this proportion must be observed in the sample taken. In sampling lumps, it is not sufficient to break pieces from the surface, but the lump should be broken, and pieces taken from both the exterior and interior, for a lump seldom has the same composition throughout. As the heavy particles that naturally find their way towards the bottom seldom have the same composition as the lighter material near the top, portions of the sample should be drawn from different parts of the lot. The fine ore should be taken up in portions amounting to about a teaspoonful, and the pieces of lumps should be about the size of cherries.

This sample will usually be too large for laboratory use, and a smaller sample must be obtained from it. Just how this is done is not a matter of importance so long as the sample obtained represents the composition of the whole quantity, but probably the best method, and the one most frequently used, is that known as quartering. This is accomplished as follows:

Break up the lumps of ore until the largest pieces are about the size of buckshot, mix the whole sample thoroughly, place it in a conical pile, and then flatten this pile. Mark the pile into quadrants, by means of a stick, as shown in Fig. 1, by passing two lines at right angles to each other through the center of it. Then remove two alternate quarters and throw them aside.. Thus considering the quadrants as numbered consecutively from *1* to *4*, Nos. *1* and *3* would be discarded, and Nos. *2* and *4* saved, or vice versa. The quadrants to be discarded may be removed by means of a spatula, shown in Fig. 2. The quadrants left are now thoroughly mixed, made into a conical pile, and the operation is repeated until a sample

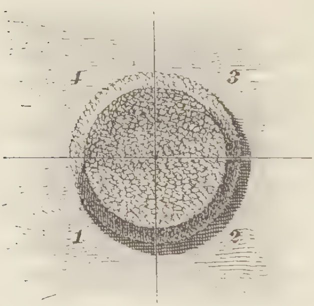

FIG. 1

of suitable size for the laboratory is obtained. If the sample contains lumps of sufficient size to cause danger of getting a final sample that does not represent the whole lot of ore, it should be broken up finer during the operation. When a sample of the proper size is obtained, it is ground to

FIG. 2

a coarse powder and mixed thoroughly. Although a cast-iron mortar and pestle are largely used in breaking up and grinding iron ores, they are totally unfit for this purpose, for the iron, especially of the pestle, rapidly wears away, and, becoming mixed with the ore, gives it a fictitious value in iron. A mortar and pestle of hardened steel, or a chilled-iron bucking board and muller, shown in Fig. 3, answer the purpose much better.

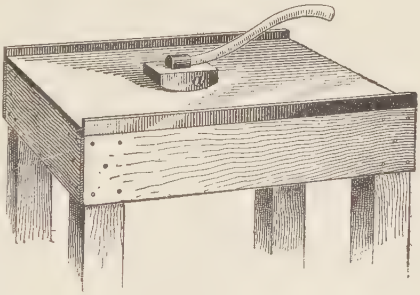

FIG. 3

The treatment of the ore from this point on differs in different laboratories. Some furnacemen want to know the exact composition of the ore as it is purchased and charged into the furnace, while others want to know the composition of the dry ore, and the chemist must regulate his method of treatment to suit the particular case. The following method probably gives the most thorough knowledge of the composition of the ore, but where such complete knowledge is not desired, the treatment may be shortened. In any case, if the moisture is to be taken into account, the ore should be ground and quartered quickly, as wet ores will lose some of their water during the operation, if much time is spent, and dry ores may take up some moisture from the atmosphere.

WATER

4. Determination of Hygroscopic Water.—Spread the ore out on a clean piece of paper, and weigh about 50 grams of it into a watch glass or other suitable vessel, dipping portions from different parts of the sample by means of a spatula. Care should be taken to dip to the bottom of the sample each time, for however well mixed it may be, this coarsely powdered sample will scarcely be uniform, the heavier portions that tend to sink to the bottom seldom having the same composition as the lighter portions on top. Place the weighed sample in an air bath, and heat it at a temperature ranging from 100° to 105° C., until it ceases to lose weight. To be sure of obtaining accurate results, this drying should be continued for 10 or 12 hours, though in many cases the water will all be driven off in much less time. When a constant weight is obtained, the loss in weight is the weight of hygroscopic water, and from this the percentage of water in the sample is obtained.

If only an analysis of the dry ore, or of the ore as it comes from the mine, is required, this determination may be omitted, and the other determinations proceeded with, either at once, or after drying, as the case may be. If this method is followed, however, by working on the same sample after it is dry, the percentage of water in the original sample and the percentage of other constituents in the dry ore are obtained; and, from these figures, the percentage of each of the constituents in the wet ore may readily be calculated.

INSOLUBLE MATTER AND SILICA

5. Grind the sample used for the determination of water in an agate mortar until it is fine enough to pass through a sieve having 100 meshes to the linear inch, commonly called a 100-mesh sieve. The whole must be passed through the sieve, for the hard particles that resist crushing seldom have the same composition as the easily pulverized portion. As soon as powdered, the sample should be placed in a bottle and tightly stoppered.

Weigh 1 gram of this sample into a porcelain dish, add 20 cubic centimeters of concentrated hydrochloric acid, cover the dish with a watch glass, and boil very gently on a hot plate or sand bath until the ore appears to be completely decomposed. A hot plate is merely a thin iron plate placed on a suitable support and heated by a burner; and a sand bath is made by placing some sand in an iron basin and heating it in the same way.

When the sample appears to be decomposed, remove the watch glass, wash any particles that may have spattered on it back into the dish, and evaporate to dryness. Or, if the solution has a tendency to bump, evaporate to dryness with the watch glass on. This requires more time, but is necessary in some cases to avoid loss by spattering. When dry, heat the residue until the odor of hydrochloric acid is no longer given off, but avoid a very high temperature. Allow the residue to cool, add about 10 cubic centimeters of concentrate hydrochloric acid, and boil for a few moments. Then add 30 or 35 cubic centimeters of water, and continue the boiling for a few minutes to dissolve all the soluble matter. Filter, preferably with suction, wash thoroughly with dilute hydrochloric acid and water alternately, and, finally, two or three times with water. Suck the precipitate and filter as dry as possible, wrap the filter around the precipitate, place them in a platinum crucible, and, after heating gently to drive off moisture and char the paper, ignite intensely over the blast lamp. Allow the crucible to become cool, and weigh as *insoluble matter* or *silicious residue*, as it is sometimes called.

To the insoluble matter in the crucible, add about ten times its weight of "fusion mixture," made by mixing equal parts of the carbonates of sodium and potassium, and heat over the blast lamp till all is in a state of quiet fusion. Run the fusion well up on the sides of the crucible, and then cool it rapidly by dipping the crucible into a porcelain dish containing about 50 cubic centimeters of pure cold water, taking care not to get any water in the crucible at first. When the fusion becomes cool enough so that there is no further danger

of spattering, turn the crucible on its side, cover the dish with a watch glass, and heat to boiling, so as to partially dissolve the fusion. Remove the dish from the flame, and complete the solution by cautiously adding concentrate hydrochloric acid until the liquid has a strong acid reaction. Remove the crucible, wash it off thoroughly, letting the washings run into the dish, evaporate to dryness on a sand bath or hot plate, and heat at a moderate temperature to render the silica insoluble. When cool, add 10 cubic centimeters of concentrate hydrochloric acid and 30 or 40 cubic centimeters of water to the residue, and boil a few minutes to dissolve the soluble matter. Filter and wash thoroughly with hot water to remove all alkaline salts from the filter. Wrap the filter around the precipitate, place them in a platinum crucible, and, after heating gently to expel moisture and char the paper, ignite intensely over a blast lamp. Cool, and weigh as silica SiO_2.

IRON

6. There are two methods of determining iron in ores in very general use, known as the bichromate and the permanganate methods. The permanganate method gives a very distinct end reaction, but as permanganate is decomposed by hydrochloric acid or chlorine, precautions must be taken to render harmless the hydrochloric acid used to dissolve the ore, before titrating the solution. Hydrochloric acid and chlorine do no harm when the bichromate method is used; hence, the ore may be dissolved in hydrochloric acid, the solution reduced by stannous chloride, and this may be titrated at once with bichromate. As each method has its advantages, they are both largely used. A method of dissolving an ore in hydrochloric acid, reducing with stannous chloride and titrating with permanganate, has recently been devised, and is being quite largely used at the present time, in some places. As it has several advantages, it will probably be more generally adopted in time, and consequently all three methods will be described.

7. The Bichromate Method.—Weigh 1 gram of the sample into a beaker, add 20 or 25 cubic centimeters of concentrate hydrochloric acid, cover the beaker with a watch glass, and digest on a sand bath for several hours, at a temperature very near the boiling point, until the ore appears to be completely decomposed. From .2 to .5 gram of potassium chlorate is frequently added at this point to oxidize any organic matter that may be present. Now raise the temperature and boil the solution very gently until its volume is reduced to about 10 cubic centimeters. With nearly all ores, the iron will now be completely dissolved, and the residue will be light colored. It should be examined, however, and if reddish, or very dark, it should be treated as described later.

If the residue is white, remove the watch glass and wash it off into the beaker, washing down the sides of the beaker at the same time, and using a quantity of water about double the volume of the solution. Then slowly add a solution of stannous chloride from a pipette or burette to the hot solution until it is colorless, indicating that the iron is all reduced to the ferrous condition, and add 2 or 3 drops in excess to be sure that reduction is complete.

After a little experience has been acquired, it is easy to tell by the appearance of the solution when reduction is complete, but at first it is best to test the solution by means of potassium sulphocyanide. To do this, place a drop of potassium-sulphocyanide solution on a white porcelain plate, known as a *spot plate*, dip a small drop of the iron solution from the beaker on the end of a stirring rod, and mix it with the drop of sulphocyanide on the plate. If a red color is produced, it shows that the solution still contains ferric iron, and more stannous chloride must be added. If it shows no color, or only a faint pink tint, the reduction is complete.

Pour the reduced solution into a rather large beaker, wash the small beaker thoroughly adding the washings to the solution, and dilute this to 300 or 350 cubic centimeters with pure cold water. Then add about 25 cubic centimeters of a saturated solution of mercuric chloride all at once, stir the

solution, and titrate with potassium bichromate, running the bichromate in until a drop of the solution, removed to a spot plate by means of a stirring rod, and mixed with a drop of pure potassium-ferricyanide solution, does not produce a blue color for 20 or 30 seconds. The operation should be conducted as rapidly as possible from the time the iron is reduced, for, if allowed to stand for any considerable time, it will be partially reoxidized by the action of the air.

The mercuric chloride is added to destroy the excess of stannous chloride, which, if left free in the solution, would reduce some of the bichromate, and thus yield an erroneous result. If it is added quickly, as directed, it will form a white, silky precipitate that does not in any way interfere with the titration, but if added gradually, a gray or black precipitate of metallic mercury is produced, and the solution must be thrown away, for such a solution will not yield reliable results. If the bichromate is standardized so that 1 cubic centimeter oxidizes .01 gram of iron, and exactly 1 gram of sample is taken, each cubic centimeter of the solution used will represent 1 per cent., and each tenth of a cubic centimeter will represent one-tenth of 1 per cent. of iron in the sample. Many chemists, however, prefer to standardize the bichromate solution so that 1 cubic centimeter of it oxidizes .005 gram of iron; and when this is done, .5 gram of ore is usually taken for the determination. If this is done, the reading in cubic centimeters will represent the percentage of iron, the same as in the first instance.

If the residue left when the ore is dissolved is strongly colored, and exact results are required, the following method should be employed: Dilute the solution slightly so that the hydrochloric acid will not destroy the paper, filter, and wash, receiving the filtrate in a beaker, which should now be covered and stood aside. Place the filter and residue in a platinum crucible, burn off the paper and fuse the residue with about ten times its weight of mixed carbonates of sodium and potassium. Dissolve the fusion in water and hydrochloric acid, filter out the insoluble matter, and wash thoroughly with dilute hydrochloric acid and water. Heat the filtrate

to boiling, add a few drops of concentrate nitric acid, and precipitate the iron with a slight excess of ammonia. Filter, dissolve the precipitate in a mixture composed of equal parts of concentrate hydrochloric acid and water, and add this solution to the main solution of iron. Heat this nearly to boiling, reduce it with stannous chloride, dilute with water, add mercuric chloride, and titrate with bichromate as directed above.

8. The Ordinary Permanganate Method.—Weigh 1 gram of the dry, finely powdered ore into a beaker, add 15 or 20 cubic centimeters of concentrate hydrochloric acid, cover the beaker with a watch glass, and digest on a sand bath or hot plate at a temperature very near the boiling point, until the ore appears to be completely decomposed. This may be accomplished in 15 or 20 minutes, or may require several hours, depending on the ore. If time permits, the sample is generally allowed to digest for several hours in any case to insure complete decomposition. If the ore contains organic matter, a little potassium chlorate should be added to destroy it, and some chemists add it to all ores as a precautionary measure. Probably the majority of ores yield all their iron to this treatment, but if the insoluble residue contains iron, it must be filtered off, fused, and treated as in the determination of iron by the bichromate method.

When decomposition is complete, unless the bulk of solution is considerably reduced, it should be boiled gently until the volume of the solution amounts to rather less than 10 cubic centimeters. Violent boiling should be avoided, as some ferric chloride may thus be volatilized from a concentrate solution. Dilute the solution with about 30 cubic centimeters of water, and, if a large residue remains, it is generally filtered off, washed thoroughly with hot water, and the filtrate and washings are collected in a flask that has a capacity equal to three or four times the volume of the solution. The residue may be fused or discarded, depending on whether it contains iron or not. The practice at this point differs, however. Some chemists prefer to filter every sample, while

others never filter the solution unless the residue contains iron, but simply wash the contents of the beaker into the flask.

In any case, to the solution in the flask add about 10 grams of pure granulated zinc, and place a small funnel in the mouth of the flask. This will catch fine drops of liquid that are carried up with the evolved hydrogen, and will protect the solution from air, while it allows the hydrogen to escape. When the reaction slackens, heat the solution gently to cause as much as possible of the acid to unite with the zinc, forming zinc chloride, which does not interfere with the titration. If a basic-iron salt begins to separate when the acid is nearly all taken up by the zinc, dissolve it in the least necessary quantity of hydrochloric acid, adding the acid drop by drop.

To the solution, which should now contain but a very small amount of free hydrochloric acid, add about 30 cubic centimeters of dilute sulphuric acid, and allow the action of the acid on the zinc to proceed for a few moments, and the iron will all be reduced. It is best, at first, to test the solution by removing a drop of it on a stirring rod, and mixing it with a drop of potassium-sulphocyanide solution previously placed on a spot plate, but after a little experience, this will be unnecessary. Pour the solution through a large fluted filter, and wash the filter by filling it once or twice with pure cold water, receiving the filtrate and washings in a large beaker or porcelain dish. Dilute this solution to 300 or 400 cubic centimeters with cold water, and titrate at once with potassium permanganate.

Many chemists do not filter the solution from the zinc, but add an excess of dilute sulphuric acid, and after the zinc is all dissolved, wash the solution into a beaker or porcelain dish, dilute, and titrate as above. When this is done, there is always danger of small particles of zinc being washed into the dish, and generating hydrogen during titration. As the hydrogen thus generated will reduce some of the permanganate, and thus yield an erroneous result, the writer prefers to filter out the zinc. The results may be obtained more quickly, and, if the filtration is performed as above directed,

the solution is not exposed to the air sufficiently to cause oxidation. By taking up most of the hydrochloric acid with zinc, and titrating the iron in a dilute solution containing considerable free sulphuric acid, the injurious effect of hydrochloric acid is overcome, and the end reaction is as sharp as if no hydrochloric acid were present.

9. The Modified Permanganate Method.—It has been found that by using a so called *titrating mixture* to counteract the evil effects of hydrochloric acid, iron may be reduced with stannous chloride and titrated with permanganate. The chief advantage of this method is the rapidity with which it yields results. Its principal disadvantage is the fact that in the hands of an inexperienced operator, the results may not be accurate, as it requires more skill and experience to make a determination correctly by this method than by either of the methods previously described. As this method is chiefly used where results must be obtained quickly, and as stannous chloride appears to aid in dissolving the ore, a little less of this than the amount required to reduce the iron is usually added at the beginning of the operation, but this is not essential. The process as usually carried out is as follows:

Weigh 1 gram of ore into a small beaker, add about 15 cubic centimeters of concentrate hydrochloric acid and a small amount of stannous chloride (about 5 cubic centimeters for ordinary ores), cover the beaker, and heat on a sand bath or hot plate until the ore is decomposed, but avoid vigorous boiling. If the ore contains organic matter, a little potassium chlorate should be added, and the heating continued until the chlorine and oxide of chlorine are expelled. Wash the cover and sides of the beaker with a jet of water from a wash bottle to bring every particle of iron into the solution, using 15 or 20 cubic centimeters of water for this purpose. Heat this solution nearly to boiling and add stannous chloride from a pipette or burette until the solution becomes colorless, showing that the iron is reduced, but avoiding the addition of more than 2 or 3 drops in excess. It is a good plan to test

this solution, to learn when reduction is complete, by removing a drop of it to a spot plate and mixing it with a drop of potassium sulphocyanide.

When the iron is all reduced, wash the solution into a large beaker or a porcelain dish with cold water, and dilute to about 100 cubic centimeters with cold water. The solution should now be quite cool. Add to it 15 cubic centimeters of mercuric chloride all at once, and stir it vigorously. Then add 50 cubic centimeters of titrating mixture (see Art. **15**), and again stir vigorously. Dilute the solution to about 600 cubic centimeters with cold water, and titrate with potassium permanganate as quickly as possible. The end reaction is a faint pink color, which must be noted quickly, as it is of short duration.

SOLUTIONS FOR IRON DETERMINATIONS

10. Standardizing Permanganate and Bichromate Solutions.—The methods of standardizing potassium-permanganate and bichromate solutions by the use of ferrous ammonium sulphate, have been given under Permanganate Method and Bichromate Method, and it is the writer's experience that solutions thus prepared yield accurate results when working on ores, provided a blank determination is made, and the amount of standard solution reduced by reagents, as determined by this blank, is deducted from the reading in each case. Most chemists, however, prefer to standardize solutions against a sample of iron, steel, or ore, the iron contents of which has been carefully determined. Piano wire is largely used for this purpose, but a standard ore has the advantage that standardization and titration are carried on under the same conditions, and in exactly the same manner. The course to be pursued in standardizing a solution for the determination of iron, by any of the methods commonly used, would readily suggest itself from what has been said on this subject under the heading Volumetric Analysis, but in order to make it more clear the method employed when a standard ore is used is given.

Dissolve the potassium permanganate or bichromate in

water, making sure that all is in solution, and then dilute until 1 liter contains, approximately, 6 grams of permanganate or 8.8 grams of bichromate, as the case may be. Mix the solution thoroughly, and, after it has stood for at least 24 hours, standardize it as follows: Dissolve exactly 1 gram of the standard ore, which we will suppose contains exactly 50 per cent. of iron, reduce the solution and titrate with the solution being prepared, following the directions given in Art. **7** for a bichromate solution, or those given in Art. **8** for a permanganate solution. Suppose 49 cubic centimeters of the solution is required to oxidize the iron in the 1-gram sample; then, each 49 cubic centimeters of this solution must be diluted to 50 cubic centimeters in order that 1 cubic centimeter shall oxidize .01 gram of iron. If the volume of the solution amounts to, say, 950 cubic centimeters, the calculation would be: $49 : 50 = 950 : x = 969.4$ cubic centimeters, the required volume, or $969.4 - 950 = 19.4$ cubic centimeters of water must be added. This should not be added all at once, however, for fear of rendering the solution too dilute. It should be diluted nearly to the calculated amount and a second determination made with the standard ore. Then dilute to the exact calculated amount, and check the solution by means of a third determination. It is always best to make duplicate determinations each time when standardizing.

If a standard solution of bichromate is to be made of such strength that 1 cubic centimeter equals .005 gram of iron, it should be diluted until 1 liter contains about 4.4 grams of the pure salt, and .5-gram samples of the standard ore should be used in the determinations. After standardizing the solutions, they should be kept in tightly stoppered bottles in a cool dark place, and should be restandardized every two weeks, as they gradually change in strength owing to slow decomposition or to other causes. It is a good plan to weigh out a sample of the standard ore, and run it with other samples at frequent intervals. Any change in the strength of the solution will thus be detected.

In iron-works laboratories, where many determinations are

made, several liters of the standard solutions are generally made up at a time. The method of preparation is, of course, the same as in the case of smaller quantities. Many chemists do not standardize their solutions so that 1 cubic centimeter oxidizes exactly .01 gram of iron, but make a solution having approximately this strength, and determine the value in iron of 1 cubic centimeter of it. Then, by multiplying the number of cubic centimeters used by the value of 1 cubic centimeter, the amount of iron is obtained, but where many determinations are made, it is an advantage to have the solution of such strength that the percentage of iron may be read directly from the burette.

11. Stannous Chloride.—Different chemists make the stannous-chloride solution, used to reduce the iron, of different strengths, varying from 25 to 150 grams of the dry salt to the liter. A very good solution for this purpose is made by dissolving 80 grams of pure stannous chloride in 500 cubic centimeters of concentrate hydrochloric acid and 500 cubic centimeters of water. The stannous chloride used for this solution should be pure and fresh, for the salt slowly decomposes on standing and forms an insoluble compound. If a pure fresh sample of the salt is not at hand, the solution may be made by dissolving pure metallic tin in concentrate hydrochloric acid and diluting to the proper volume with pure water. If this is done, it is best to place a piece of platinum foil in contact with the tin, to promote solution, which is very slow at best.

12. Mercuric Chloride.—The mercuric-chloride solution, used to oxidize the excess of stannous chloride is generally made by dissolving 50 grams of the salt in 1 liter of water. This makes very nearly a saturated solution, and the reagent is frequently made by adding water to a little more of the salt than it will dissolve, thus keeping a little undissolved salt in the bottle. If this is done, the solution should be shaken up frequently to keep the undissolved salt from forming a hard cake that is not readily dissolved in water.

13. Potassium Sulphocyanide.—The potassium-sulphocyanide solution, used in testing for ferric iron, to learn when reduction is complete, is made by dissolving from 5 to 10 grams of the salt in 100 cubic centimeters of water.

14. Potassium Ferricyanide.—The potassium-ferricyanide solution, used as an indicator in determining iron by the bichromate method, is made by dissolving about .5 gram of the pure solid ferricyanide in 100 cubic centimeters of water. The ferricyanide must be free from ferrocyanide, for this gives a blue color with ferric iron. It may be tested by mixing a drop of it with a drop of ferric solution that is known to be free from ferrous compounds. This solution is slowly reduced by the light, and, consequently, a fresh solution should be made up every day, or at least every second day.

15. Titrating Mixture.—To make the titrating mixture, used when iron is reduced by stannous chloride and titrated with permanganate, dissolve 160 grams of manganous sulphate in water and dilute the solution to 1,750 cubic centimeters; then add 330 cubic centimeters of 85-per-cent. phosphoric acid, and, finally, stir in 320 cubic centimeters of sulphuric acid of 1.84 Sp. Gr. By using this mixture, iron may be titrated with permanganate in a cold dilute solution containing hydrochloric acid, and satisfactory results obtained, if the titration is performed rapidly.

PHOSPHORUS

16. As the percentage of phosphorus varies greatly in different ores, and as ores differ in solubility, the exact method employed for the determination of this element varies with different ores. Another cause of variation in the details of the method, is the fact that, while, as a rule, exact results are required, it sometimes happens that rapidity is of more importance than extreme accuracy, and in such cases the method is shortened to suit the conditions. As exact results are usually required, a very accurate method

is here described, and if the student should need a more rapid method at any time, he can readily work out a method that will meet his requirements, after studying the determination of phosphorus in iron and steel. In working out a shorter method, the student should remember that the solution from which the ammonium phospho-molybdate is precipitated should have as near as possible the same composition in every case, for the composition of this precipitate varies slightly in different solutions, and if the solution is too strongly acid, the phosphorus will not be completely precipitated; while from an alkaline solution it will not be precipitated at all.

If the ore contains a very high percentage of phosphorus, 1 gram of the sample should be used for this determination, while with ores containing a very low percentage of this

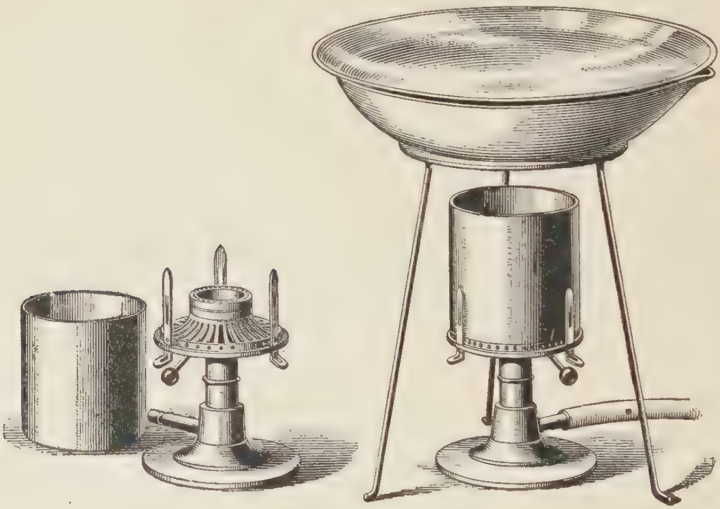

FIG. 4

element, 10 grams are usually taken. The quantity of acid used to dissolve the ore varies with the amount of sample taken, but not in a direct proportion. To dissolve 1 gram of ore, 25 cubic centimeters of acid should be used, while 100 cubic centimeters will be sufficient for 10 grams. This

determination usually proves a stumbling block to the beginner, and, consequently, the directions should be followed as closely as possible until the student becomes familiar with it. After a little practice, however, it becomes very easy to obtain extremely accurate results. The details of the method as used for ordinary ores are as follows:

Weigh 5 grams of the finely powdered sample into a porcelain dish, add 1 cubic centimeter of nitric acid and 75 cubic centimeters of concentrate hydrochloric acid, cover the dish with a watch glass, and digest on a sand bath, a hot plate, or on a tripod placed over an Argand burner, shown in Fig. 4, until the ore appears to be completely decomposed. Then evaporate to dryness, and, to render the silica insoluble, ignite the residue at a moderate temperature until the odor of hydrochloric acid is no longer perceptible. When the residue becomes cool, add 50 cubic centimeters of concentrate hydrochloric acid, heat gently until the mass dissolves, then raise the temperature and boil the solution down to about 20 cubic centimeters. Add 30 cubic centimeters of water, boil for a few moments, filter off the insoluble matter, wash thoroughly with hot water, and stand the filtrate aside. The insoluble residue will seldom contain more than a trace of phosphorus, and, with most ores, in cases where rapidity is of greater importance than extreme accuracy, it may be discarded. As a rule, however, it should be treated as follows:

Place the filter and residue in a platinum crucible and burn off the paper, mix the residue with five or six times its weight of the mixed carbonates of sodium and potassium, and heat till all is in a state of quiet fusion. After cooling, dissolve the fusion in water and hydrochloric acid, and evaporate to dryness in a porcelain dish. Moisten the residue with concentrate hydrochloric acid, again evaporate to dryness, and ignite gently until the odor of hydrochloric acid can no longer be observed. When cool, add from 5 to 10 cubic centimeters of concentrate hydrochloric acid to the residue, heat gently for a few moments, then add 25 cubic centimeters of water, heat to boiling, and filter. Hear the

filtrate to boiling, add a few drops of concentrate nitric acid, and then a slight excess of ammonium hydrate. Any phosphorus that may have remained in the insoluble residue will be carried down in the precipitate thus formed. Filter, wash two or three times with hot water, dissolve the precipitate in the least necessary quantity of hydrochloric acid, and add this solution to the main filtrate, which will now contain all the phosphorus originally in the sample.

Evaporate this solution in a porcelain dish until it becomes syrupy, and the scale of iron oxide that forms on the sides of the dish is only dissolved slowly, but take care not to evaporate the solution until a scale forms that is not dissolved by agitating the solution. Now remove the dish and contents from the flame, immediately add 7 or 8 cubic centimeters of concentrate nitric acid, and, after rotating the dish a few times to mix the solution, wash down the watch glass and sides of the dish with water. Transfer the solution, which must not contain any undissolved matter, to a flask of about 700 cubic centimeters capacity, and wash out the dish, using water enough to bring the volume of the solution up to about 100 cubic centimeters.

To this solution add 30 cubic centimeters of concentrate ammonia, and, after giving the flask a rotary motion to mix the contents, dissolve the precipitate in concentrate nitric acid, adding about 2 cubic centimeters in excess of the amount actually required to give a clear solution. Insert a thermometer in the solution, bring its temperature to exactly 85°, add 75 cubic centimeters of ammonium-molybdate solution, and agitate the mixture for 5 minutes by giving the flask a sharp rotary motion. The phosphorus is thus completely precipitated as ammonium phospho-molybdate, generally known as *yellow precipitate*, which, when precipitated as directed above, contains 1.63 per cent. of phosphorus. Allow the precipitate to settle, which will usually require 15 or 20 minutes, but do not allow it to stand more than 1 hour. Filter and wash the precipitate with water acidified with nitric acid until the iron is completely removed, filling the filter from six to ten times.

The precipitate is next dissolved in ammonia. It is best to dissolve it on the filter and allow the solution to run through into a clean beaker and wash the filter thoroughly. If the silica and iron have been thoroughly removed, as directed above, this is not necessary, however, and the precipitate may be washed into a beaker and dissolved in ammonia. In either case, bring the volume of the solution to about 80 cubic centimeters, add magnesia mixture in considerable excess, and dissolve the precipitate formed in the least necessary quantity of hydrochloric acid. Stand the beaker containing the solution in ice water and slowly add concentrate ammonia while stirring the solution vigorously.

After the solution is rendered alkaline, add about 25 cubic centimeters of concentrate ammonia, stir vigorously and stand aside in a cool place for at least 3 hours for the precipitate to collect and settle. It is a good plan to allow it to stand overnight. Filter, wash the precipitate thoroughly with a dilute solution of ammonia (1 part of concentrate ammonia to 3 parts of water) containing 5 grams of ammonium nitrate in each 100 cubic centimeters of solution, and dry it in an air bath. Remove the precipitate as completely as possible from the filter and burn the latter in a platinum crucible. When cool, add the precipitate, ignite strongly over the blast lamp, cool in a desiccator, and weigh. The precipitate will now generally consist of pure magnesium pyrophosphate $Mg_2P_2O_7$, which contains 27.93 per cent. of phosphorus, but as a little silica may be present, it is best to make a correction as follows:

Fill the crucible to half its capacity with nitric acid of 1.2 Sp. Gr., apply heat until chemical action ceases, and, if an insoluble residue remains, filter it off, wash thoroughly, ignite strongly in a platinum crucible over the blast lamp, and weigh. By deducting this weight from that of the original precipitate, the weight of magnesium pyrophosphate is obtained, and from this the percentage of phosphorus is calculated.

As the percentage of phosphorus in the ammonium phospho-molybdate, precipitated as above directed, is known, this

precipitate may be weighed or titrated by one of the methods described for the determination of phosphorus in iron or steel; but as the gravimetric method in which the phosphorus is finally weighed as magnesium pyrophosphate is the only one that yields exact results in every case, this method should be employed whenever extreme accuracy is required.

SOLUTIONS FOR PHOSPHORUS DETERMINATIONS

17. Ammonium Molybdate Solution.—There are many formulas for making this solution, and several of these that the writer has tried have proved very satisfactory. The following formula is a very good one, where large quantities of the solution are used. If the student wishes to make up a smaller amount of the solution, he can use smaller quantities of the constitutents, keeping the proportion the same, of course.

Mix 700 cubic centimeters of ammonia (Sp. Gr. .90) with 1,325 cubic centimeters of water. Dissolve in this 500 grams of molybdic anhydride MoO_3. Mix 2,415 cubic centimeters of nitric acid (Sp. Gr. 1.42) with 4,000 cubic centimeters of water. Allow the two solutions to cool, and if any impurities remain undissolved, filter the molybdate solution. When both solutions are cool, pour the molybdated solution slowly into the nitric acid, stirring constantly. Do not pour the nitric acid into the molybdate. In laboratories having an air blast, the agitation may be accomplished by passing a current of air through the solution. When all is added, stand the solution in a warm place for 24 hours, and decant the clear solution, or filter before using. When this solution is to be used for the volumetric determinition of P_2O_5, 5 cubic centimeters of strong nitric acid should be added to each 100 cubic centimeters and the solution filtered before using.

18. Magnesia Mixture.—The magnesia mixture for this purpose is frequently made as follows: Dissolve 110 grams of pure crystallized magnesium chloride and 280 grams of ammonium chloride in 1,300 cubic centimeters of

water. To this add 700 cubic centimeters of ammonia of .96 Sp. Gr., shake well, allow to stand several days, and filter before using.

19. Nitric-Acid Wash.—To make the dilute nitric acid used in washing the "yellow precipitate," measure 15 or 20 cubic centimeters of concentrate nitric acid (Sp. Gr. 1.42) into a wash bottle, fill up to 1 liter with pure water and shake well. The solution is generally made to contain 20 cubic centimeters of nitric acid to the liter, but some chemists prefer a more dilute solution.

SULPHUR

20. Sulphur occurs in iron ores both in the form of sulphides and sulphates. It must all be obtained in the form of a soluble sulphate, and precipitated as barium sulphate by means of barium chloride. In the case of most ores, the sulphur may be obtained in the form of a soluble sulphate, either by treating the ore with hydrochloric and fuming nitric acids, or by fusing it with the mixed carbonates of sodium and potassium and potassium nitrate. The fusion method is the only one that yields accurate results in all cases, but as the treatment with acids is the handiest in cases where it is admissible, both methods are given.

21. The Aqua-Regia Method.—Weigh 5 grams of the ore into a rather deep porcelain dish, cover it with a watch glass, and slowly add 20 cubic centimeters of fuming nitric acid. When the action nearly ceases, add 30 cubic centimeters of concentrate hydrochloric acid, and allow it to stand at the temperature of the laboratory for a short time—an hour or two, if time permits. Transfer to a water bath or a sand bath, and digest at a gentle heat until the ore appears to be decomposed. Then add 1 gram of sodium carbonate dissolved in 10 cubic centimeters of water, raise the temperature, and evaporate to dryness. In order to render the silica insoluble, moisten the residue with concentrate hydrochloric acid,

again evaporate to dryness, and ignite gently until the odor of hydrochloric acid is no longer given off.

When cool, add 10 cubic centimeters of concentrate hydrochloric acid, heat for a few moments, then add 50 cubic centimeters of water and boil till solution is complete. Filter off the insoluble matter, and wash with hot water until the soluble material is completely removed from the paper, and the volume of the solution amounts to from 150 to 200 cubic centimeters. Heat the solution to boiling, add a moderate excess of barium chloride (25 cubic centimeters of a 5-per-cent. solution is sufficient for most ores), and continue the boiling for several minutes. Stand the solution on a water bath or other warm place for an hour, then stand it in a cool place till the precipitate has completely settled and the solution is cool.

Filter, preferably, through a Gooch crucible. When the solution has run through, fill it up with hot water, and when this has run through, wash once with hot dilute hydrochloric acid, and then wash thoroughly with hot water. Suck the water out of the asbestos as completely as possible, dry, and ignite it at a dull-red heat for 5 minutes, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur. If a filter paper is used instead of a Gooch crucible, the precipitate should be removed from it as completely as possible, and the paper burned cautiously before the precipitate is ignited.

22. The Fusion Method.—Mix 1 gram of the pulverized ore with about 6 grams of sodium and potassium carbonates, and .5 gram of potassium nitrate; introduce this mixture into a large platinum crucible and cover it with a mixture of about 2 grams of the mixed carbonates, and .25 gram of potassium nitrate. Cover the crucible and heat it at a gradually increasing temperature until the mass is in a state of quiet fusion, but do not ignite longer than necessary, as this mixture is likely to injure the crucible if the heating is continued too long. Run the fusion well up on the sides of the crucible and cool it rapidly by dipping it in

cold water, taking care not to let any water get inside of the crucible. When cool, place the crucible and contents in a porcelain dish, add about 100 cubic centimeters of water, and boil to dissolve the fused mass. When the fusion is loosened from the crucible, remove it, and wash it off into the dish by means of a wash bottle. If any hard lumps remain in the solution, they may be broken up by gently rubbing with a pestle, which must afterwards be washed off into the dish.

When the fusion is completely disintegrated, allow the undissolved portion of iron, etc. to settle, and, if the solution has a green or red tint, add a few drops of alcohol to precipitate the manganese, which causes this color. Filter, and wash the precipitate thoroughly with hot water, collecting the filtrate and washings in a porcelain dish. Render the filtrate distinctly acid by the cautious addition of concentrate hydrochloric acid, evaporate to dryness, and ignite gently to render the silica insoluble. Moisten the residue with 5 cubic centimeters of concentrate hydrochloric acid, add from 50 to 75 cubic centimeters of water, and heat until the sodium salts are completely dissolved. Filter, and wash thoroughly with hot water, bringing the volume of the filtrate to about 150 cubic centimeters. Heat this filtrate to boiling, add 10 cubic centimeters of a 10-per-cent. solution of barium chloride (or 20 cubic centimeters of a 5-per-cent. solution), and continue the boiling for several minutes.

Stand the solution in a warm place for from 4 to 6 hours for the precipitate to collect and settle in a coarse granular form, filter, wash thoroughly with hot water, and dry in an air bath. Remove the precipitate as completely as possible from the filter and burn the latter in a weighed crucible. Moisten the ash with a drop of nitric and a drop of sulphuric acid, heat gently at first, and then raise the temperature to faint redness to drive off the excess of acid. Add the precipitate, heat to dull redness for 5 minutes, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur.

If preferred, the barium sulphate may be filtered on a Gooch felt, but, when this method is employed, the precipitate

is generally obtained in a form so coarse that it does not run through a filter, and, consequently, the use of a Gooch crucible is not necessary. It is frequently advised to heat the barium chloride, used to precipitate the sulphur, to boiling before adding it, in order to obtain the precipitate in a coarser form; but if the boiling is continued for some minutes after the addition of the barium chloride, this is unnecessary.

MANGANESE

23. More or less manganese is found in nearly all iron ores, and its determination is often a matter of importance. The two methods that are probably the most used are Volhard's method and Ford's method. Both these methods have been more or less modified by different chemists, and they are given here, not exactly as they were originally described by their authors, but as they are most frequently used in practical work.

Volhard's method is quite rapid and simple, and it is the writer's experience that it yields accurate results in all cases. Many chemists, however, do not consider it accurate for ores containing less than .5 per cent. of manganese, and Ford's method is generally considered the more reliable of the two. Hence, although it is longer, Ford's method is generally used when exact results are required, especially if the ore contains but little manganese. Both these methods may be used for manganese ores as well as for the ores of iron.

24. Volhard's Method.—Weigh 1.5 grams of the sample into a porcelain dish, add 20 cubic centimeters of concentrate hydrochloric acid, about 10 drops of concentrate nitric acid, and 15 cubic centimeters of dilute sulphuric acid (1 part of acid of 1.84 Sp. Gr. to 2 parts of water). Evaporate to dryness on a hot plate, and ignite till dense white fumes of sulphur trioxide are given off. When cool, add about 75 cubic centimeters of water, and boil until the sulphates are completely dissolved. Wash the solution into a 300-cubic-centimeter graduated flask, cool the solution, add a strong solution

of sodium carbonate until the solution is almost neutral and assumes a red color, but no precipitate forms; then add an emulsion of zinc oxide in water until the color becomes light brown, generally described as the color of coffee with cream.

Dilute exactly to the mark with pure water, and mix thoroughly. Pour this mixture on a large, dry, fluted filter, placed in a dry funnel, and receive the filtrate in a dry clean beaker. By means of a pipette, transfer 200 cubic centimeters of this filtrate, which represents 1 gram of ore, to a flask, and heat it to boiling. As soon as the solution commences to boil, remove it from the source of heat, run in a little standard potassium-permanganate solution, give the flask a sharp rotary motion to cause the precipitate to collect, allow it to partly settle and note the color of the solution. If the solution is colorless, add more permanganate, shake the flask, allow the precipitate to partially subside, note the color of the solution, and continue this treatment until the supernatant liquid shows a pink color after the precipitate has settled. This titration must be rapidly performed, so as to allow little time for the solution to cool.

When a potassium-permanganate solution is added to a solution of manganese sulphate at about the boiling point, the manganese in both solutions is precipitated according to the equation:

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + 2KHSO_4 + H_2SO_4$$

When all the manganese in the manganese-sulphate solution is precipitated, the excess of permanganate added gives the solution a pink tint, which indicates the end of the reaction. Knowing the strength of the permanganate solution, the amount of manganese in the sample is readily calculated from the above equation. If the ore contains a very high percentage of manganese, it is best to dilute the 200 cubic centimeters of solution, withdrawn after filtering, to some exact volume, depending on the amount of manganese present; and then take 200 cubic centimeters of this solution for titration.

25. Ford's Method.—Weigh 1 gram of ore into a porcelain dish, add 25 cubic centimeters of concentrate hydrochloric acid and evaporate to complete dryness, but avoid a temperature much above 100°. Add 5 cubic centimeters of concentrate hydrochloric acid and 20 cubic centimeters of water to the residue, and boil till the chlorides are all in solution. Filter off the silica, wash it thoroughly with hot water, and evaporate the filtrate to dryness, but avoid ignition. Dissolve the residue in concentrate nitric acid, and boil the solution down until it is almost syrupy, to expel hydrochloric acid. Add 50 cubic centimeters of concentrate nitric acid, boil for a few minutes, and then add, a little at a time, from 5 to 8 grams of potassium chlorate to oxidize the manganese and precipitate it as manganese dioxide MnO_2. When enough has been added to oxidize the manganese, the greenish-yellow vapors above the solution will give a puff and disappear. Now add about 1 gram more of potassium chlorate and boil about 2 minutes; then cool rapidly by standing the beaker in cold water, and, when it is cold and the precipitate has settled, filter through an asbestos filter.

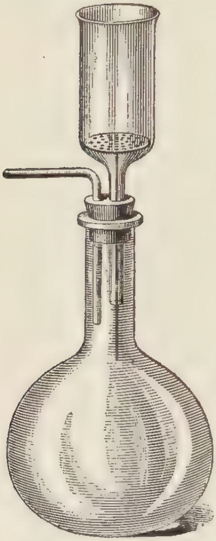

FIG. 5

To make a filter for this purpose, a perforated porcelain disk, such as is used with a porcelain Gooch crucible, is attached to a stout platinum wire and placed in a filtering tube fitted in a filtering flask, as shown in Fig. 5. Pour the asbestos suspended in water into the tube, and, by means of the pump, draw the water through, depositing the asbestos on the disk, forming a filter, or "plug," as it is generally called. If a disk and wire for this purpose are not at hand, an irregular piece of glass, or a piece of pumice stone, may be placed in the neck of the filtering tube, and the asbestos deposited on it.

Wash the beaker and precipitate twice with concentrate nitric acid by pouring 15 or 20 cubic centimeters of it into the beaker in which the precipitation was accomplished, and, after running it around in the beaker, pour it on the precipitate and draw it through the plug. When all has passed through the filter, repeat the operation. The acid used for washing the precipitate must be pure and colorless; if it is colored by nitrous fumes, which are always developed in nitric acid that is allowed to stand in the light, it will dissolve the manganese dioxide; but acid thus colored may be purified by passing a current of air through it.

By pressing on the end of the platinum wire extending through the bottom of the filtering tube, force the precipitate and asbestos out into the beaker in which the precipitation was made; or, if a platinum wire were not used, the precipitate and plug may be forced out by means of a thin stirring rod. Add about 30 cubic centimeters of strong sulphurous acid (made by leading sulphur dioxide into water) and 5 cubic centimeters of hydrochloric acid, pouring the acids through the filtering tube to dissolve any precipitate that may be adhering to it. Stir the precipitate and asbestos up with a glass rod, and the acid mixture will rapidly dissolve the manganese dioxide. Filter to remove the asbestos, and wash it well on the filter with hot water. Boil the filtrate until the excess of sulphur dioxide is driven off, add a few drops of concentrate nitric acid, and, after boiling a few moments longer, add a slight excess of ammonium hydrate to precipitate the iron present. Filter, wash several times with hot water, and stand the filtrate aside. Dissolve the precipitate on the filter with hydrochloric acid, allow the solution to run through and wash the filter well with hot water, receiving the solution and washings in a clean beaker. Heat the solution to boiling, reprecipitate the iron with ammonia, filter, and wash the precipitate thoroughly with hot water.

Unite the two filtrates, which will now contain all the manganese freed from other metals, and the volume of which should amount to about 300 cubic centimeters. Add a rather

large excess of microcosmic-salt solution (from 20 to 50 cubic centimeters, according to the amount of manganese present) and dissolve the precipitate thus formed in the least necessary quantity of concentrate hydrochloric acid. Heat the solution to boiling, and, while keeping it as near as possible to the boiling point, add concentrate ammonia, drop by drop, until the last drop causes a permanent precipitate. Now stop the addition of ammonia, and stir the solution vigorously until the precipitate assumes a silky crystalline appearance; then add another drop or two, stir again, and continue this treatment until the manganese is all precipitated in the crystalline condition. Then add 2 or 3 cubic centimeters of the ammonia in excess, and stir well. Stand the beaker in a cool place until the solution is cool and the precipitate has completely settled.

It may be filtered after standing 20 minutes, but if there is no hurry, it is best to allow it to stand 2 hours. Filter and wash thoroughly, but not excessively, with water made slightly alkaline with ammonia, and containing 100 grams of ammonium nitrate to the liter. Dry in an air bath, remove the precipitate as completely as possible from the filter, and burn the latter in a weighed crucible. Add the precipitate, ignite intensely over the blast lamp, cool in a desiccator, and weigh as manganese pyrophosphate $Mn_2P_2O_7$, which contains 38.73 per cent. of manganese.

SOLUTIONS FOR MANGANESE DETERMINATIONS

26. Zinc Oxide.—The zinc-oxide emulsion, used to precipitate the iron in Volhard's method, is prepared by mixing pure zinc oxide with water until it has a creamy consistency. The zinc oxide separates out on standing, and, consequently, it must be shaken thoroughly before it is used.

27. Potassium Permanganate.—The standard permanganate solution, used in titrating iron, may be used for this determination by making a calculation. The manganese is precipitated according to the equation:

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + 2KHSO_4 + H_2SO_4$$

Hence we see that 2 molecules of permanganate, which oxidize 10 molecules of ferrous sulphate, only oxidize 3 molecules of manganese sulphate. Taking the atomic weights of iron and manganese as 56 and 55, respectively, we have $\frac{55}{56} \times \frac{3}{10} = \frac{33}{112}$, or .2946. That is, the value of the permanganate solution in iron, multiplied by .2946, gives its value in manganese, or the value of a permanganate solution in manganese is 29.46 per cent. of its value in iron.

It is best, however, if many determinations are to be made, to make, for this purpose, a solution of permanganate of such strength that the percentage of manganese may be read directly from the burette, and this plan is universally adopted in iron-works laboratories where this method is used. If the solution titrated represents one gram of ore, the permanganate solution should be made of such strength that 1 cubic centimeter of it oxidizes .001 gram of manganese, corresponding to .1 per cent. The method of standardizing will be readily understood from the above calculation.

PIG IRON

28. As pig, or cast, iron is the first product in the manufacture of iron and steel, its analysis will be treated next. The principal determinations, and, in fact, the only determinations frequently made, are four in number; viz., *silicon*, *sulphur*, *phosphorus*, and *manganese*. As all these elements tend to segregate to a greater or less extent, pig iron is never homogeneous; a single pig will not have exactly the same composition throughout, and, if samples are taken from different parts of a cast, the variation will be still greater; hence the selection of a sample becomes a matter of importance. If a cast is to be sampled, probably the best method is to remove three samples of the molten iron, as it runs from the furnace, by means of a ladle, taking the first sample soon after the iron begins to run, the second when about half of it has passed out, and the third towards the end of the cast. After these test pieces have cooled, break them, drill an equal amount from the interior of each piece, and mix the drillings.

A sample is thus obtained that, as a rule, quite closely represents the composition of the whole cast.

If a car of metal is to be sampled, pigs should be taken from different parts of the car, then broken, and mixed with the same quantity of drillings taken from the interior of each pig. This method should also be employed in sampling a pile of iron.

Iron drillings are always likely to contain sand and scale, and these must be removed before weighing up a sample. This is best done as follows: Spread the drillings on a clean paper, place another paper over them and bring a magnet in

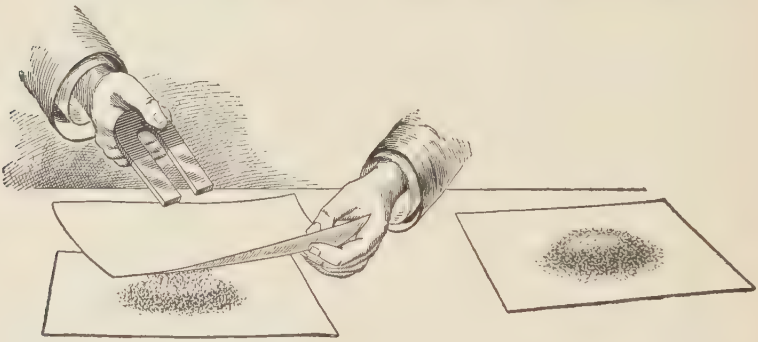

FIG. 6

contact with this paper. By lifting up on the magnet, which attracts the drillings and holds them close to the paper, remove part of the drillings and hold them over another clean paper. Then by holding the paper between the magnet and drillings firmly, and withdrawing the magnet, allow the drillings to fall on the paper placed to receive them. By repeating this a few times, all the drillings will be removed to the second paper, while the sand and scale, being non-magnetic, will remain on the first. The method of accomplishing this is illustrated in Fig. 6. Now, after mixing the sample thoroughly to get a uniform mixture of coarse and fine drillings, which usually differ somewhat in composition, the sample is ready to be weighed out for the different determinations.

It should be mentioned at this point that a short piece of thick iron wire, ground to a point and magnetized, is very handy in transferring small particles of the sample to and from the weighing glass on the pan of the balance.

SILICON

29. Drown's Method.—For this determination, the method proposed by Dr. Drown, or a slight modification of the same, is almost universally adopted. The method, as it is probably most frequently employed, is as follows: Weigh 1 gram of drillings into a porcelain dish, cover the dish with a watch glass, and add 20 cubic centimeters of nitric acid of 1.2 Sp. Gr., drawing the glass aside to admit the acid. If the drillings are very fine, the acid should be added cautiously to prevent loss during solution. When violent action ceases, add 15 cubic centimeters of dilute sulphuric acid (1 part of acid to 2 parts of water), evaporate to dryness on a hot plate, or over the bare flame of an Argand burner, and continue to heat until copious white fumes of sulphur trioxide are given off.

If the heat is carefully regulated, the evaporation may be accomplished without spattering, but as there is always more or less danger, it is best to keep the dish covered with a watch glass to catch any particles that may spatter against it, and would otherwise be lost, and to boil the solution down rapidly. When cool, add 15 cubic centimeters of dilute hydrochloric acid (equal parts of acid and water, generally spoken of as 1 : 1 acid), then from 30 to 50 cubic centimeters of water, and boil vigorously until the sulphates are completely dissolved. Wash any precipitate adhering to the watch glass into the solution, and, after allowing it to stand a few moments for the precipitate to settle, filter while still quite warm, preferably with the aid of a filter pump. Wash twice with hot water, then fill the filter with warm dilute hydrochloric acid (generally 1 : 1), and when this has passed through, continue to wash with hot water until the iron is completely removed from the precipitate

and filter. The precipitate now consists of silica and graphite. Wrap the filter around it, place them in a platinum crucible, and, after igniting moderately to burn the paper, heat at the full power of the blast lamp until the graphite is burned off, leaving the precipitate perfectly white. When cool, weigh as silica SiO_2, which contains 47.02 per cent. of silicon.

The results obtained as just directed are accurate enough for all practical purposes, but, if absolute accuracy is required, add 2 or 3 drops of sulphuric acid to the silica after weighing it; then dissolve it in hydrofluoric acid, evaporate to dryness, ignite, cool, and weigh the residue, if any, remaining in the crucible. The difference between the two weights is the weight of silica which has been expelled by heating the hydrofluoric-acid solution. When many determinations are made daily, this method is frequently modified as follows: Weigh .9404 gram of the sample into a porcelain dish, dissolve it in 25 cubic centimeters of mixed acids (made up in the proportion of 18 parts of nitric acid of 1.2 Sp. Gr. to 7 parts of half-strength sulphuric acid), evaporate to dryness, and heat until dense white fumes of sulphur trioxide are given off. When cool, dissolve the sulphates in hydrochloric acid and water, filter, wash, ignite (usually in a muffle furnace), and weigh. As .9404 is twice the factor weight (.4702) of silicon, the weight of silica divided by 2 is the percentage of silicon. When precipitates are ignited in a muffle furnace, they are usually placed, together with the filter, in a platinum crucible that is supported on a tripod of platinum wire, as shown in Fig. 7. The crucible standing in the tripod is placed in a muffle maintained at a white heat until the precipitate is white, then it is removed and is weighed as soon as cool. As twenty-five or thirty precipitates may be ignited at one time in a muffle, much time is saved by this method of ignition if many determinations are being made.

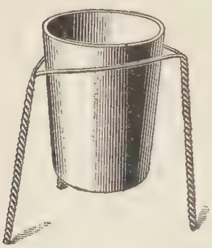

FIG. 7

SULPHUR

30. A number of methods for the determination of sulphur in iron have been proposed, but only two, known as the *evolution method* and the *aqua-regia method*, are used very extensively in iron-works laboratories. The evolution method depends on the fact that all the sulphur in iron exists in the form of sulphide, and can ordinarily be evolved in the form of hydrogen sulphide by treating the sample with hydrochloric acid. By the aqua-regia method, the sulphur is oxidized to sulphate, and is precipitated and weighed as barium sulphate.

The evolution method is rapid and simple, and with most samples yields extremely accurate results. Occasionally, however, a sample is met that will not yield all its sulphur by this method; hence, in settling disputes, and in establishing standards, the aqua-regia method should always be employed.

31. The Evolution Method.—Weigh 5 grams of drillings into a flask having a capacity of 750 or 800 cubic centimeters, and close the flask with a doubly perforated stopper. Through one of the perforations of this stopper pass a funnel tube with a stop-cock, reaching nearly to the bottom of the flask, and, through the other, pass a short delivery tube bent at right angles, over the end of which a short piece of rubber tubing is tightly fitted. Place a tight-fitting, doubly perforated rubber stopper in a test tube containing an ammoniacal solution of cadmium chloride, and through one perforation pass a glass tube reaching nearly to the bottom of the test tube, and connect this with the rubber tube attached to the delivery tube of the flask. Through the other perforation pass the short limb of a tube bent twice at right angles, so that it reaches just through the stopper, and pass the longer limb nearly to the bottom of a second test tube, fitted like the first. Each tube should contain 25 cubic centimeters of cadmium-chloride solution and 25 cubic centimeters of water. Fit the flask in a suitable support over an Argand burner. The test tubes may be supported by the tube connecting them.

The arrangement of the apparatus will be understood from Fig. 8. Close the apparatus, and pour from 90 to 100 cubic centimeters of hydrochloric acid (1 : 1) into the funnel tube. Then turn the stop-cock, allowing the acid to run into the flask, and, as soon as it is all in, close it again. The iron is rapidly dissolved with the evolution of hydrogen, and the sulphur, which is in the form of sulphide, is evolved as hydrogen sulphide. The gases pass through the test tubes containing cadmium chloride where the hydrogen sulphide is absorbed with the formation of cadmium sulphide.

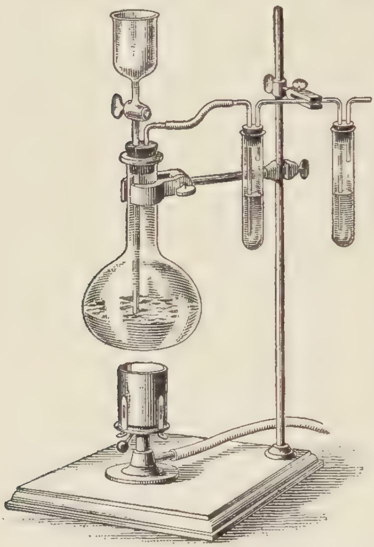

FIG. 8

When the evolution of gas slackens, light the burner under the flask, and turn it low until the iron is all dissolved; then raise the temperature and boil the solution until all hydrogen sulphide is expelled and the solution in the first test tube is quite warm from the steam passing over from the flask. Now open the stop-cock of the funnel tube, turn out the light, and disconnect the rubber tube connecting the flask and test tubes. Remove the test tubes, pour their contents into a beaker, and thoroughly wash the test tubes and tubes leading into them, allowing the washings to run into the solution in the beaker, which is then diluted to about 300 cubic centimeters. Add about 5 cubic centimeters of starch solution, render the solution distinctly acid with hydrochloric acid, and titrate at once with a standard solution of iodine.

When the solution is rendered acid with hydrochloric acid, hydrogen sulphide is formed, and this reacts with the iodine according to the equation:

$$H_2S + I_2 = 2HI + S$$

This reaction takes place as long as the solution contains hydrogen sulphide, but as soon as this is consumed, the iodine commences to unite with the starch, forming blue starch iodine; hence the appearance of a permanent blue color indicates the end of the reaction. The solution must be titrated immediately after it is acidified, or the hydrogen sulphide formed will partly escape, and the results obtained will be too low. For the same reason, the acid used to acidify the solution should be added quickly.

In iron-works laboratories, a series of supports is generally arranged over stationary Argand burners, which are much better than Bunsen burners for this purpose; but for practice, or for an occasional determination, the apparatus shown in Fig. 8 serves very well, and in such cases a Bunsen burner or even an alcohol lamp may be substituted for the Argand burner.

32. The Aqua-Regia Method.—Weigh 5 grams of drillings into a porcelain dish, or, still better, a porcelain beaker, and quickly add 50 cubic centimeters of nitric acid of 1.42 Sp. Gr., so that the sample is completely covered at once. If rapid solution commences at once, stand the porcelain dish in cold water to check the action. If the sample does not begin to dissolve in a few moments, add a few drops of concentrate hydrochloric acid, and heat it gently. Violent action may be checked by standing the dish in cold water, preferably, ice water.

About 10 cubic centimeters of hydrochloric acid should be added in small portions during the solution. When this is all in, and the sample is dissolved, add about $\frac{1}{2}$ gram of potassium chlorate and 1 gram of sodium carbonate, evaporate to dryness, and ignite slightly. Dissolve the residue in 20 or 25 cubic centimeters of concentrate hydrochloric acid, evaporate to dryness, and again ignite gently to render the silica insoluble. Dissolve the residue in 25 or 30 cubic centimeters of concentrate hydrochloric acid, and evaporate until the solution becomes syrupy; then add 5 cubic centimeters more of concentrate hydrochloric acid, and heat

gently till the solution becomes clear. Dilute this solution with a little more than twice its own volume of hot water, mix thoroughly, filter through a paper that has previously been washed with hot dilute hydrochloric acid, and wash the filter thoroughly with hot water, adding a few drops of hydrochloric acid, if necessary, to remove red stains from the paper.

Heat the filtrate, which should amount to about 200 cubic centimeters, to boiling, add 20 cubic centimeters of a 5-per-cent. solution of barium chloride, or 10 cubic centimeters of a 10-per-cent. solution, and continue the boiling a few minutes. Stand the solution in a warm place for at least 2 hours; then filter, and wash thoroughly on the filter with hot water, acidulated with a few drops of hydrochloric acid. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a weighed crucible. Add 1 or 2 drops each of concentrate nitric and sulphuric acids, evaporate to dryness, and ignite gently to expel the excess of acid. When cool, add the precipitate, heat to dull redness, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur.

A Gooch crucible may be used instead of a filter paper in filtering the barium sulphate, and is preferred by many chemists on account of the tendency of the precipitate to pass through a filter, and the ease with which it is reduced when ignited in the presence of carbonaceous matter.

In the case of some samples of iron containing a high percentage of sulphur, a small quantity of this element appears to escape oxidation when the sample is dissolved as above directed. In such cases, it is best to stand the dish containing the sample in cold water, add the nitric acid quickly so that the drillings are entirely covered at once, and allow the dish to stand in the cold water about an hour. Then add 10 cubic centimeters of concentrate hydrochloric acid, and allow the dish to stand in a cool place several hours longer before applying heat to effect solution. In this way, much of the sulphur is oxidized before there is

any apparent action, and the results obtained are slightly higher, in some cases, than when the sample is dissolved in the usual manner.

SOLUTIONS FOR SULPHUR DETERMINATIONS

33. Cadmium-Chloride Solution.—This solution is made up as follows: Dissolve 100 grams of cadmium chloride in 500 cubic centimeters of water and 500 cubic centimeters of concentrate ammonia, and filter through a fluted filter into a large bottle. To the filtrate add 2 liters of concentrate ammonia and 2 liters of water, and mix thoroughly. Generally for the absorption, a single test tube 1 inch in diameter and 10 or 12 inches in length, with a delivery tube reaching to the bottom, is used. About 25 cubic centimeters of the cadmium solution, diluted to about 100 cubic centimeters, are introduced into the tube, and the determination proceeded with as directed. It is safer, however, to divide this solution between two test tubes, as directed.

Instead of the cadmium solution one of zinc may be used. This may be prepared by dissolving 70 grams of zinc oxide in hydrochloric acid, using only enough hydrochloric acid to decompose the oxide. Add 500 cubic centimeters of concentrate ammonia, and filter if necessary. Add 2 liters of strong ammonia and 2 liters of water; mix thoroughly. This solution is used in the same way as the cadmium solution, and has been found equally as satisfactory.

Some chemists use a solution of potassium hydrate to absorb the H_2S. A good strength of this solution is got by dissolving 200 grams KOH in water and diluting to 1,000 cubic centimeters. When using this solution the amount of hydrochloric acid required to render acid the amount of KOH solution used should be determined, and this amount of acid added before titrating. With the cadmium and zinc solutions, the disappearance of the odor of ammonia shows that the solution is acid; but with the potash solution it is best to measure the acid.

34. Starch Solution.—To make the starch solution for the indicator, mix from 5 to 10 grams of pure starch with

40 or 50 cubic centimeters of water; pour this into a liter of boiling water, and continue the boiling a few moments, meanwhile stirring with a glass rod. Allow the solution to settle, and decant the clear liquid for use. A fresh solution should be made up at least once a week.

35. Standard Iodine Solution.—The iodine solution is made of such strength that 1 cubic centimeter represents .0005 gram of sulphur, or .01 per cent. of sulphur when 5 grams of sample are taken. The reaction between hydrogen sulphide and iodine is

$$H_2S + I_2 = 2HI + S$$

or 254 grams of iodine set free 32 grams of sulphur. Hence, in order that 1 cubic centimeter of the solution shall repsent .0005 gram of sulphur, 1 liter of it must contain 3.969 grams of iodine.

It is common practice to standardize the iodine solution against a steel of known sulphur content. This is done as follows: Dissolve 10 or 12 grams of potassium iodide in from 50 to 75 cubic centimeters of cold water, add 4 grams of freshly sublimed iodine, stir till all is dissolved, and dilute to about 1 liter. Then dissolve 5 grams of the standard steel in half-strength hydrochloric acid, absorb the hydrogen sulphide in cadmium chloride, as directed in Art. **31**, and titrate with this solution. From the result thus obtained, calculate how much the solution must be diluted, add the calculated amount of water and mix thoroughly. Then make another determination, using the standard steel, to be sure that the solution is right. This solution should be kept in a dark, cool place and should be restandardized once a week.

As potassium bichromate liberates iodine from its compounds, an iodine solution may be made up and standardized at the same time by the use of a standard solution of potassium bichromate. The reaction is as follows:

$$K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + 2CrCl_3 + 7H_2O + 3I_2$$

Hence, 1 cubic centimeter of a decinormal solution of

potassium bichromate, which oxidizes .0056 gram of iron, liberates .0127 gram of iodine, and 312.5 cubic centimeters liberate 3.969 grams of iodine. The solution is made up as follows:

Dissolve about 15 grams of potassium iodide in 200 cubic centimeters of water. Then dilute 10 cubic centimeters of concentrate hydrochloric acid to 200 cubic centimeters, add this to the potassium-iodide solution, and, from a burette, run in 312.5 cubic centimeters of decinormal bichromate solution while stirring continuously. Dilute this solution to exactly 1 liter and mix it thoroughly, when it will be ready for use.

The same volume of a decinormal solution of potassium permanganate may be used instead of the bichromate by substituting sulphuric for hydrochloric acid. If this is done, pour 10 cubic centimeters of concentrate sulphuric acid into 200 cubic centimeters of water, and, after this solution has cooled, slowly pour it into the potassium-iodide solution while stirring continuously. Add 312.5 cubic centimeters of decinormal permanganate solution to this, and proceed as with the bichromate. The reaction in this case is as follows:

$$2KMnO_4 + 10KI + 8H_2SO_4$$
$$= 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

PHOSPHORUS

36. A number of methods for the determination of phosphorus in pig iron are in general use. In most of these methods, the phosphorus is first precipitated as ammonium phospho-molybdate, generally spoken of as "yellow precipitate," and the various methods differ principally in the treatment of the yellow precipitate.

37. Obtaining the Yellow Precipitate.—Weigh 5 grams of the drillings into a porcelain dish, cover with a watch glass, and add 70 cubic centimeters of nitric acid of 1.2 Sp. Gr. When violent action ceases, place the dish on a tripod over an Argand burner, which is turned very low

until solution is complete. This will usually require about half an hour. Now raise the temperature, evaporating to dryness as rapidly as possible, and ignite the residue until acid fumes are no longer given off. The carbonaceous matter is thus destroyed, and the phosphorus is oxidized to phosphate. When cool, add 35 cubic centimeters of concentrate hydrochloric acid and heat gently till the residue is dissolved; then raise the temperature, and evaporate as rapidly as possible, with the cover on, until the solution becomes syrupy, thus expelling as much hydrochloric acid as possible without having iron salts separate.

Remove the dish from the burner, add 20 cubic centimeters of concentrate nitric acid, boil down to about 8 cubic centimeters, this should drive off the rest of the chlorine; then, without delay, wash any iron solution adhering to the watch glass and the sides of the dish down into the main solution, using from 75 to 100 cubic centimeters of warm water, and stir the solution well. Filter into a flask having a capacity of about 700 cubic centimeters, and wash the filter and residue thoroughly with a 2-per-cent. solution of nitric acid. To the solution in the flask add 30 cubic centimeters of concentrate ammonia, shake the flask until the precipitate becomes smooth, then add enough concentrate nitric acid to dissolve it, forming a clear amber-colored solution.

Suspend a thermometer in the solution, bring its temperature to exactly 85°, add 75 cubic centimeters of ammonium molybdate, and agitate the contents of the flask for 5 minutes by giving the flask a rotary motion, or by shaking it. The phosphorus will now be completely precipitated as ammonium phospho-molybdate. After allowing it to settle for 15 or 20 minutes, filter and determine the phosphorus in it by one of the following methods.

38. Weighing as Magnesium Pyrophosphate.—Wash the yellow precipitate thoroughly with 2-per-cent. nitric acid, dissolve it in ammonia, precipitate the phosphorus as magnesium-ammonium phosphate, ignite strongly, and weigh as

magnesium pyrophosphate, following the directions given in Art. **16.**

This method is much longer than some of the others, but, as it is probably the most reliable of any, it is largely used in settling disputes, and in other cases where extreme accuracy is required.

39. Titration With Permanganate.—Wash the precipitate thoroughly with an acid ammonium-sulphate solution, place the funnel in the neck of a 500-cubic-centimeter flask, spread the filter on the side of the funnel, or break its apex with a glass rod, and wash as much of the precipitate as convenient into the flask with water. To dissolve the precipitate adhering to the paper, pour dilute ammonia over it, and wash the paper thoroughly with water, allowing all the solution to run into the flask.

Enough ammonia should be added to dissolve all the yellow precipitate, both on the filter and in the flask, but a large excess should be avoided. Pour 15 grams of granulated zinc into the flask, add 100 cubic centimeters of dilute sulphuric acid (made by adding 1 part of concentrate acid to 3 parts of water), place a small funnel in the neck of the flask and heat gently for half an hour, when reduction will be complete.

Pour the contents of the flask, which should still contain some undissolved zinc, upon a large folded filter, receiving the filtrate in a large beaker. Rinse out the flask with water, and, as soon as the main solution has passed through, pour this on the paper. When these washings have passed through, fill the filter once with cold water, and, as soon as this passes through, titrate the solution with potassium permanganate.

As the permanganate is added to the solution, it gradually changes color, and finally becomes colorless. A few additional drops of the permanganate will now impart a faint pink to the solution, indicating that the reaction is complete. From the amount of permanganate used, the percentage of phosphorus in the sample is obtained.

40. Titration With Nitric Acid.—Wash the yellow precipitate four times with a 2-per-cent. solution of nitric acid, and then four times with a 1-per-cent. solution of potassium nitrate. Remove the filter containing the yellow precipitate to a beaker, add standard sodium-hydrate solution in sufficient quantity to completely dissolve the precipitate, and stir with a glass rod until the filter paper is broken up into a pulp. About 30 cubic centimeters of the standard sodium hydrate will usually be sufficient. It should be added from a burette, and the amount used should be carefully noted. Dilute the solution to 75 or 100 cubic centimeters with water, add a few drops of phenol-phthalein, and titrate with a standard solution of nitric acid that exactly matches the standard sodium hydrate. The quantity of sodium hydrate used to dissolve the precipitate, minus the amount of nitric acid required to neutralize the excess of sodium hydrate, gives the amount of sodium hydrate actually needed to dissolve the precipitate, and, from this, the percentage of phosphorus is calculated.

41. Weighing the Yellow Precipitate.—As ammonium phospho-molybdate, precipitated as above directed, contains 1.63 per cent. of phosphorus, it may be weighed, and the phosphorus thus determined. If this method is employed, filter through a paper that has been dried at 110° in an air bath for 1 hour, and weighed quickly between matched glasses. Wash the precipitate from six to ten times with a 2-per-cent. solution of nitric acid, place the filter containing the precipitate on a piece of porcelain in an air bath, dry for 1 hour at 110°, and weigh quickly between matched glasses. The increase over the first weight is the weight of the yellow precipitate, and as this contains 1.63 per cent. of phosphorus, the percentage of phosphorus in the sample is readily calculated from this weight.

SOLUTIONS FOR PHOSPHORUS DETERMINATIONS

42. Acid Ammonium Sulphate.—To make up the acid ammonium-sulphate solution used in washing the yellow precipitate, add 27 cubic centimeters of concentrate ammonia

to $\frac{1}{2}$ liter of water; then slowly add 25 cubic centimeters of concentrate sulphuric acid, and dilute the solution to 1 liter with cold water. After mixing the solution well, and allowing it to cool, it is ready for use.

43. Standard Potassium Permanganate.—When the yellow precipitate is acted on by nascent hydrogen, generated by the zinc and sulphuric acid, the molybdic oxide is reduced to a lower oxide, the exact composition of which is still in doubt, but which appears to be $Mo_{12}O_{19}$. When permanganate is added to this, the molybdenum is oxidized to molybdic oxide again, probably according to the equation:

$$5Mo_{12}O_{19} + 34KMnO_4 = 60MoO_3 + 17K_2O + 34MnO$$

At all events, 34 molecules of $KMnO_4$ produce 60 molecules of MoO_3. From this we see that 2 molecules of permanganate, which oxidize 560 parts of iron, will produce 508.23 parts of MoO_3 from the reduced oxide; or, the strength of a permanganate solution in terms of molybdic oxide is 90.76 per cent. of its strength in terms of iron. As the yellow precipitate contains 1.794 per cent. as much phosphorus as molybdic oxide, the strength of the permanganate solution in terms of phosphorus is 1.628 per cent. of its strength against iron. From this the percentage of phosphorus may readily be calculated when the titration is performed with any permanganate solution of known strength. In practical work, however, it is much more convenient to make a permanganate solution of such strength that 1 cubic centimeter = .006141 gram of iron. Its strength against molybdic oxide is 90.76 per cent. of this, or .005574 gram, and its strength against phosphorus is 1.794 per cent. of this, or .0001 gram.

To make such a solution, dissolve .8597 gram of ferrous ammonium sulphate, which contains .12282 gram of iron, in 150 cubic centimeters of water and 15 cubic centimeters of concentrate sulphuric acid, titrate with the permanganate, and dilute until just 20 cubic centimeters are required to oxidize the iron in this quantity of ferrous ammonium

sulphate. To make the permanganate solution, dissolve 3.5 grams of pure potassium permanganate in water, dilute to a little less than 1 liter, and let it stand in a cool dark place 2 or 3 days before the first titration. When this is diluted until 20 cubic centimeters of it just oxidize .12282 gram of iron, 1 cubic centimeter of it represents .0001 gram of phosphorus. After standardizing the solution in this way, it is best to test it against a standard steel or iron in which the phosphorus has been repeatedly determined gravimetrically, by weighing as magnesium pyrophosphate.

44. Sodium Hydrate and Nitric Acid.—Ammonium phospho-molybdate is a precipitate of varying composition; but when prepared as described, it has a composition represented by the formula $(NH_4)_3PO_4(MoO_3)_{12}$, which when dried at a low temperature retains 1 molecule of water and therefore contains 1.63 per cent. phosphorus. Sodium hydrate decomposes it according to the following reaction:

$$2(NH_4)_3PO_4(MoO_3)_{12} + 46NaOH$$
$$= 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 22H_2O$$

Since 46 molecules of sodium hydrate correspond to 2 molecules of ammonium phospho-molybdate, and therefore to 2 atoms of phosphorus, it follows that for every atom of phosphorus 23 molecules of sodium hydrate are required. It was seen in *Quantitative Analysis*, Part 2, that a normal solution of sodium hydrate contains in 1 liter the molecular weight, in grams, of $NaOH$. If, then, we have a sodium-hydrate solution 23 times as strong as a normal solution, it will contain sufficient sodium hydrate to correspond to 31 grams phosphorus per liter, or .031 gram of phosphorus per cubic centimeter. Such a solution is obviously far too strong. As a solution 1 cubic centimeter of which corresponds to .0002 gram phosphorus is desired, calculate the strength of the solution required in terms of a normal solution by the proportion $.031 : .0002 = 23 : x$. $x = .1483$. Therefore, a solution .1483, or 14.83 per cent., normal is the one required.

The solid sodium hydrate almost always contains some

carbonate. The solution required here should contain no carbonate, and it is best to prepare a strong stock solution as follows: Dissolve about 80 grams sodium hydrate in 500 cubic centimeters of water, add to this a saturated solution of barium hydrate as long as a precipitate forms. Transfer to a bottle having a rubber stopper, dilute to 1 liter, stopper tightly, shake the bottle, and allow the precipitate to settle. While this is settling prepare, according to the methods given in *Quantitative Analysis*, Part 2, a 14.83-per-cent. normal nitric acid.

When the barium carbonate has completely settled in the stock solution of sodium hydrate, draw off 200 cubic centimeters of the clear solution, dilute to 2 liters, mix thoroughly, and determine its strength against the 14.83-per-cent. normal nitric acid. Then continue the dilution until the sodium hydrate is the same strength as the nitric acid, and is therefore 14.83 per cent. normal. Each cubic centimeter of this solution corresponds to .0002 gram phosphorus.

While, as a rule, many chemists standardize the alkali solution against a weighed amount of pure ammonium phosphomolybdate, or against a standard sample of iron in which the phosphorus has been carefully determined and that is obtained through one of the standard laboratories, others, for reasons of their own, prefer the method given.

MANGANESE

45. The three methods most frequently used for the determination of manganese in iron are Ford's method, Volhard's method, and the color method. Ford's method is regarded as the most reliable, and is very largely used in settling disputes, establishing standards, etc., but it is too long to be very largely used in doing the routine work of an iron-works laboratory. Volhard's method, if properly carried out, yields very accurate results, and is sufficiently short to be largely employed in routine work. The color method is not generally considered as reliable as the other methods in the case of iron, but, on account of the rapidity with which

it yields results, it is quite largely used as a guide in manufacturing processes, and, in the hands of an experienced chemist, it yields very satisfactory results.

46. Ford's Method.—Dissolve 5 grams of the drillings in 65 cubic centimeters of nitric acid of 1.2 Sp. Gr., and boil until the solution becomes almost syrupy; then add 100 cubic centimeters of nitric acid of 1.42 Sp. Gr., boil for a few moments, and add from 5 to 10 grams of potassium chlorate to the boiling solution, a little at a time, to precipitate the manganese as dioxide. When precipitation is complete, the greenish-yellow gas above the liquid gives a puff and disappears. Now add 1 gram more of potassium chlorate, boil 1 or 2 minutes, and cool rapidly by standing the beaker in cold water. When the solution has become cold and the precipitate has settled, filter through asbestos, and from this point proceed as directed in Art. **25.**

47. Volhard's Method.—Dissolve 1.5 grams of the drillings in a porcelain dish in 25 cubic centimeters of nitric acid of 1.2 Sp. Gr., and when the violent action ceases, add 12 cubic centimeters of half-strength sulphuric acid; evaporate to dryness, and ignite until dense white fumes of SO_3 are given off. Allow the residue to cool, add 100 cubic centimeters of water, and boil until solution is complete. When cool, wash the solution into a 300-cubic-centimeter graduated flask, nearly neutralize the acid with a concentrate solution of sodium carbonate, and add an emulsion of zinc oxide in water until the mixture assumes the color of coffee with cream. Dilute with water to exactly 300 cubic centimeters, mix thoroughly, and pour the solution through a large fluted filter placed in a dry funnel, receiving the filtrate in a clean dry beaker. By means of a pipette, transfer 200 cubic centimeters of this solution to a 500-cubic-centimeter flask, heat to boiling, and titrate with potassium permanganate, shaking it well after each addition of permanganate, to cause the precipitate formed to collect and settle rapidly. A pink tinge in the clear liquid above the precipitate indicates the

end of the reaction. The titration must be rapid, so that the solution has no chance to cool.

48. The Color Method.—Weigh out .2 gram of standard iron in which the manganese has been carefully determined, and pour it into a 10-inch test tube; then place exactly the same weight of the sample to be tested in a similar test tube, and dissolve each in 25 cubic centimeters of nitric acid of 1.2 Sp. Gr. When violent action ceases, stand the tubes on a sand bath heated by a good burner, or suspend them over Argand burners, and, after solution is complete, boil them gently until the yellowish fumes are entirely expelled from the tubes. Then add about 2 grams of lead peroxide to each and continue the boiling for 3 minutes. The lead peroxide oxidizes the manganese to permanganic acid, which has the well known color of potassium permanganate. Cool the solutions rapidly by standing the test tubes in cold water.

When the solutions are cool, and the insoluble matter has completely settled, decant the standard into a graduated reading tube having an inside diameter of about $\frac{1}{2}$ inch, and dilute it until each cubic centimeter of the solution represents .01 per cent. of manganese. For example, if the standard iron contains .3 per cent. of manganese, dilute the solution to 30 cubic centimeters. Then decant the solution to be tested into a similar reading tube, and dilute it until it has exactly the same color as the standard. Each cubic centimeter of this solution will then represent .01 per cent. of manganese; thus, if the solution is diluted to 35 cubic centimeters to make the colors agree, the sample contains .35 per cent. of manganese. If care is taken in decanting the solutions from the test tubes to the reading tubes, all but 2 or 3 drops of the liquid may be decanted without introducing any of the insoluble matter.

Instead of heating the samples over a burner or on a sand bath, the tubes are sometimes stood in a solution of calcium chloride that boils at 115°. In this way, the solutions may be boiled without danger of breaking the tubes. It is scarcely

necessary to add, that, in order to obtain correct results, the standard and the sample to be tested must be treated in as near the same manner as possible.

CARBON

49. Carbon is not usually determined in pig iron, but occasionally the percentage of this element is required. When this is the case, it is determined by one of the combustion methods given under Steel, using 1 gram of the sample and a corresponding amount of solvent. The color method for carbon is not applicable in the case of pig iron.

STEEL

50. Although steel is usually more regular than pig iron in composition, it is still far from homogeneous in many instances, and, consequently, in taking a sample, drillings from different parts of the piece sampled should be obtained if possible. The bottom of an ingot seldom has exactly the same composition as the top, and the center of a rod or wire usually differs in composition from the metal at the surface. These irregularities in composition should always be taken into account when selecting a sample for analysis. A sample of steel is not so likely to contain sand as is pig iron, but it may contain scale, and, if this is present, the sample should be freed from it by means of the magnet, as in the case of pig iron.

The principal determinations made in the analysis of steel are *silicon*, *sulphur*, *phosphorus*, *manganese*, and *carbon*. Silicon is less frequently determined than the other elements, but its estimation is important in some cases. Sulphur and manganese are determined in steel in exactly the same way that they are estimated in iron, and, as the determination of these elements in pig iron has been thoroughly described, they will not be treated at this point. It should be stated, however, that the color method for manganese is considered more reliable in the case of steel than when

applied to pig iron. In fact, for the routine work in steel-works laboratories, it is used much more than any other method.

It is frequently stated that the color method is only accurate for samples containing less than 1 per cent. of manganese, but chemists that have used this method largely, usually regard it as reliable in the case of all samples containing less than 2 per cent., and some experiments seem to show that it will yield satisfactory results with samples containing even higher percentages. A standard steel, having, approximately, the same percentage of manganese as the sample tested, should always be used; hence, it is best to have several standards containing different quantities of manganese. Sometimes samples of iron are compared with a steel standard, but, as a rule, it is best to compare samples of steel with a steel standard, and samples of iron with an iron standard. Aside from what has just been said, in determining sulphur and manganese in steel, the directions given for the determination of these elements in iron should be followed exactly.

SILICON

51. Weigh 5 grams of the drillings into a porcelain dish, cover it with a watch glass, add 50 cubic centimeters of nitric acid of 1.2 Sp. Gr., and 35 cubic centimeters of half-strength sulphuric acid, and evaporate rapidly over an Argand burner until the solution begins to bump; then turn out the flame, remove the cover, and stir the syrupy solution vigorously for a few moments, when it will solidify. Or, after adding the acid, stand the dish on a sand bath, with the cover drawn to one side, and allow it to slowly evaporate to dryness. In either case, heat the residue over an Argand burner until dense white fumes are given off. When cool, add 30 cubic centimeters of half-strength hydrochloric acid and about 75 cubic centimeters of water; heat until solution is complete, and boil the solution a few minutes to make sure that all iron salts are dissolved. Filter through a small ashless filter, wash first with half-strength hydrochloric

acid, then once with water, then again with half-strength hydrochloric acid, and, finally, wash five or six times with water. Wrap the filter around the precipitate, place them in a platinum crucible, and, after burning off the paper, ignite intensely over a blast lamp. Cool in a desiccator and weigh as silica SiO_2, which contains 47.02 per cent. of silicon.

Sometimes a correction is made as follows: Dissolve the precipitate of SiO_2 in hydrofluoric acid, add 2 or 3 drops of sulphuric acid, evaporate to dryness, ignite, cool, and weigh again. If the determination is properly performed, this is unnecessary, for, in this case, the result obtained by the correction will seldom, if ever, differ from the first result; and, if there is a difference, it will be very slight.

PHOSPHORUS

52. The phosphorus in steel may be determined by any of the methods described for the determination of this element in iron, and one of these methods is generally employed. In addition to these, however, Dr. Drown has proposed a method in which the phosphorus is oxidized and the organic matter destroyed by potassium permanganate in a nitric-acid solution, and, on account of its rapidity, this method is quite largely employed. Other methods of oxidizing the phosphorus in solution have also been proposed, but none of these have come to be used so generally as that proposed by Dr. Drown. It has been stated that some samples of steel—notably, those containing a high percentage of carbon—do not yield all their phosphorus when oxidized by any of these wet methods, but this objection does not appear to be proven. Dr. Drown's method yields very accurate results with ordinary steel, and many chemists consider it perfectly reliable in all cases. Others, however, prefer to use one of the methods given for the determination of phosphorus in iron, until the objection mentioned has been more thoroughly investigated. These methods are applied to steel in exactly the same way that they are to iron.

53. Drown's Method.—Weigh 2 grams of the drillings into a 12 or 16 ounce Erlenmeyer flask, add 75 cubic centimeters of nitric acid of 1.13 Sp. Gr., and, after violent action ceases, boil the solution for 2 or 3 minutes. Add 10 cubic centimeters of a potassium-permanganate solution containing about 12 grams to the liter, and continue the boiling until the pink color of the permanganate is destroyed. If the solution becomes clear, more permanganate must be added, and the boiling continued until a brown precipitate forms, when oxidation of phosphorus and carbon will be complete. Remove the flask from the heat for a moment, and add pure ferrous sulphate, in very small portions, until the precipitate is nearly dissolved; then boil it again for a few moments until the solution becomes perfectly clear. Remove the flask from the heat, and, after a minute or two, cautiously add 10 cubic centimeters of ammonia of .90 Sp. Gr., allowing the ammonia to run down the side of the flask, to avoid loss by spattering.

Boil the solution again for a few moments, to completely dissolve the iron precipitate; then insert a thermometer and allow the solution to cool to 85°. When at exactly this temperature, add 50 cubic centimeters of ammonium-molybdate solution, causing it to rinse off the thermometer as it flows into the flask. Give the flask a rotary motion for a few moments, then close it with a clean rubber stopper, and shake vigorously for 5 minutes. Allow the precipitate to settle for 15 minutes, filter, and wash thoroughly with the acid ammonium-sulphate solution described in Art. **42.** Wash as much of the precipitate as is convenient into the flask in which the precipitation was made, and dissolve the portion adhering to the paper with dilute ammonia, adding enough ammonia to dissolve all the precipitate; then wash the filter thoroughly with water, allow the ammonia and washings to run into the flask with the main part of the precipitate, and stir this until the precipitate is completely dissolved.

To this solution add about 12 grams of granulated zinc and 80 cubic centimeters of dilute sulphuric acid (1 part of

concentrate acid to 3 parts of water), place a small funnel in the neck of the flask, and stand it in a warm place for half an hour. Reduction will now be complete. Pour the solution through a large fluted filter, to separate the undissolved zinc. Rinse the flask with pure cold water, pour this on the filter, and, when it has run through, wash the filter by filling it once or twice with pure cold water. The filtrate, which should amount to from 300 to 400 cubic centimeters, is titrated at once with permanganate. As the permanganate is added, the solution gradually changes color and finally becomes colorless, when a few more drops of permanganate will impart a pink tinge to it, showing that the reaction is complete.

The solutions used in this determination are the same as those employed for the determination of phosphorus in iron, and the calculations are the same, except, in this case, 2 grams of the sample are taken.

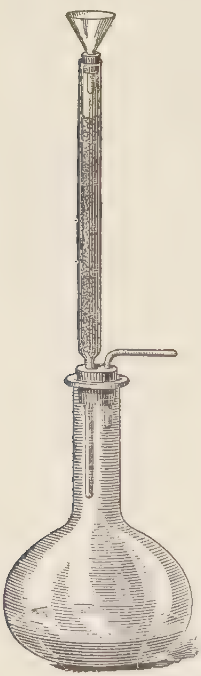

FIG. 9

This method is frequently modified by passing the solution of the yellow precipitate through a reductor instead of reducing it by heating in a flask with zinc and sulphuric acid.

54. The Reductor.—At the present time, chemists are beginning to use a reductor quite largely to reduce solutions. A simple form of reductor is shown in Fig. 9. It is made as follows: Draw out a piece of glass tubing having an inside diameter of about $\frac{1}{2}$ inch; cut it off at a point about 15 inches from the end, and pass the small portion of the tube thus drawn out through one of the perforations of a rubber stopper fitted in a filtering flask. Drop in a few pieces of broken glass that are too large to pass through the small part of the tube, and, on this,

pour about 1 inch of coarse quartz sand that has been thoroughly cleansed (first, by boiling in hydrochloric acid, and then washing with distilled water) and thoroughly dried. On this, pour about 12 inches of pure granulated zinc that will pass through a 20-mesh but not through a 30-mesh sieve, and close the tube with a singly perforated stopper through which the stem of a funnel is passed. When a solution containing acid is poured in the funnel and drawn through the column of zinc, it is completely reduced at once, and, after washing the zinc thoroughly, is ready for titration.

To use the reductor in the determination of phosphorus by the method just given, dissolve the yellow precipitate in ammonia as directed, add about 50 cubic centimeters of dilute sulphuric acid (1 part acid to 3 parts water), dilute to 200 cubic centimeters, pour it in the funnel and draw it through the reductor by means of the filter pump. Wash all the solution out of the reductor by drawing 200 cubic centimeters of water through it, and titrate the solution at once with permanganate. The reagents used destroy some permanganate, and the amount thus used up must be determined by means of blanks, and deducted from the amount of permanganate used in the titrations. Several blanks, containing, approximately, the same amount of each of the reagents, and about the same amount of free acid, and having, approximately, the same bulk as the solution to be titrated, should be passed through the reductor and titrated. The first blank will generally use more permanganate than the succeeding ones; if this is the case, this result should be discarded, and the average of the others taken as the amount of permanganate to be deducted in each case.

CARBON

55. Unlike any of the other elements contained in steel, carbon is known to exist in at least two conditions in the metal, in forms known as *graphite* and *combined carbon*. It is also believed that the combined carbon exists in two modifications, which are known as *hardening* and *cement*

carbon, and recent investigations have made this view appear almost certain.

It was noticed that when steel was worked, the results obtained in determining the combined carbon by the color method differed during the working, and that the properties of the steel also differed. It appears that the carbon shown by the color method is the part of this element present that imparts to the steel the property of becoming hard when tempered, and has received the name of hardening carbon. The color method is used almost exclusively for the determination of carbon in the routine work of steel-works laboratories, and, as the amount of graphite in steel is very small, and cement carbon, if such a form exists, is not known to have any influence on the properties of the metal, the results obtained by this method are usually reported merely as *carbon*.

From what has been said, it is evident that analytical chemistry supplies the means of distinguishing between at least two forms of this element in steel; viz., combined carbon and graphite, and it now seems probable that the color method only gives a part of the combined carbon, known as *hardening carbon*. For a long time the results obtained by the color method were supposed to represent all the combined carbon, and at present the percentage thus obtained is usually spoken of as the *combined carbon*. Accurate combustion methods are used for the determination of the total carbon, and the graphite; and from these results, the combined carbon is obtained by difference.

Three combustion methods are given. The first one—burning the carbonaceous residue in oxygen—is the most generally used, but the apparatus is costly, and the results obtained by the other methods, the apparatus for which is less expensive, are almost, if not quite, as accurate.

The carbon is not very often determined in pig iron, but if desired, either of the combustion methods here given may be used equally well for this purpose. In determining the carbon in pig iron, spiegeleisen, etc., 1 gram of sample and a corresponding amount of solvent should be used.

Otherwise, the determinations should be carried out exactly as here given.

56. Total Carbon.—Weigh out 3 grams of the fine drillings, add 200 cubic centimeters of an acid solution of the double chloride of copper and potassium, and stir until the copper thrown out at first is all redissolved. The solution may be accomplished in a beaker, a 16-ounce Erlenmeyer flask, or a heavy glass jar. The drillings should be very fine for this determination, for fine drillings yield more uniform results, and, with coarse drillings, the process of solution becomes very tedious. If necessary, a few more drops of acid may be added, and the mixture heated to 80°. When the copper is all taken up by the solution, allow it to stand a few minutes to settle, and then proceed by one of the following methods:

1. *Combustion in Oxygen.*—Filter on a felt of pure ignited asbestos in a platinum boat shown in Fig. 10, leaving as much of the carbon as possible in the vessel. Add 10 cubic

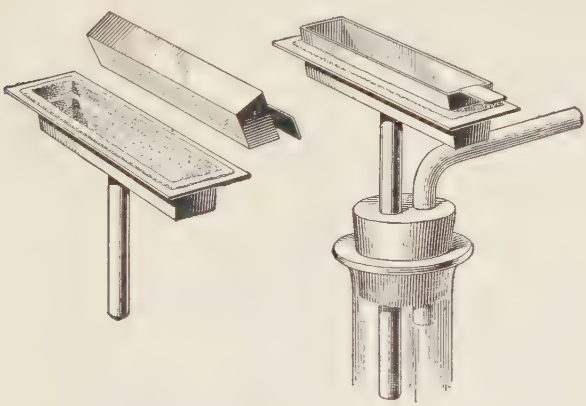

FIG. 10

centimeters of hydrochloric acid of 1.1 Sp. Gr. to the vessel in which the sample was dissolved, and so manipulate that this acid shall touch every part of the vessel that has come in contact with the solvent liquid. Pour this acid on the felt in the boat, wash the carbon upon the felt by means of

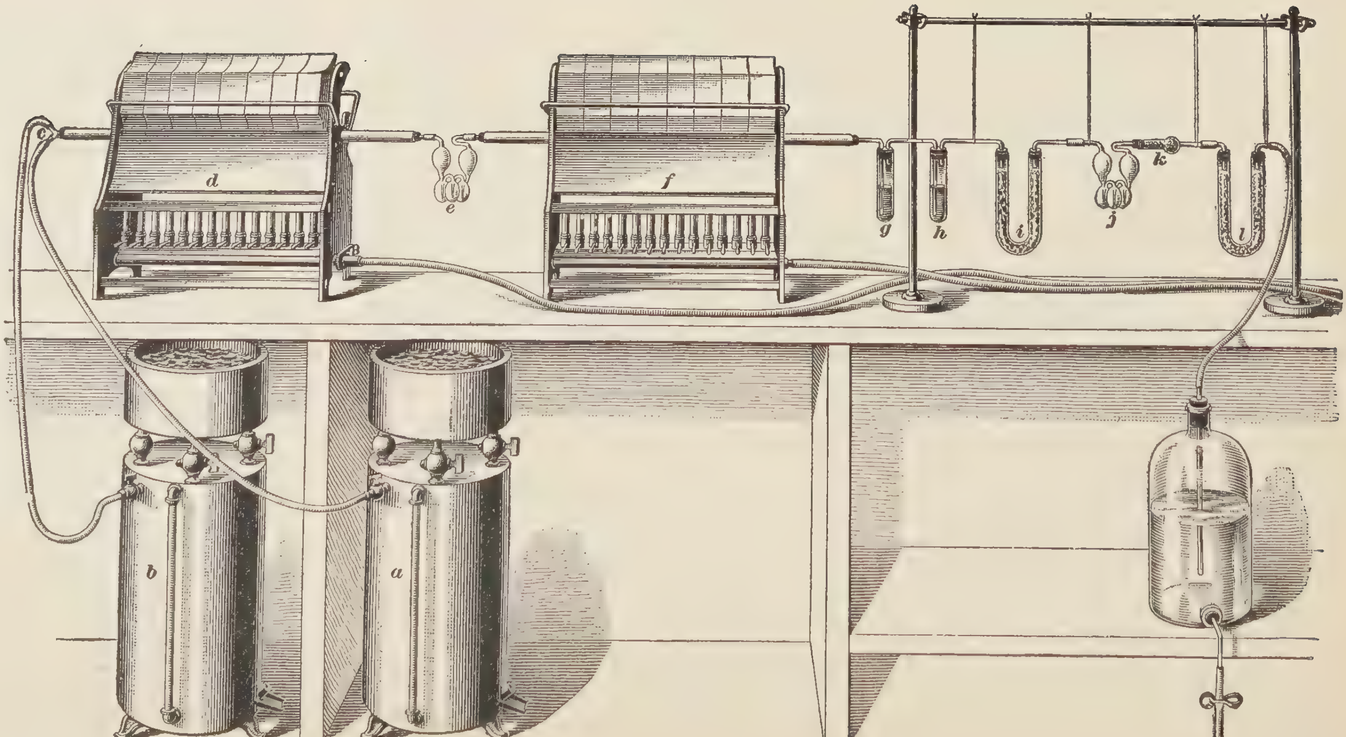

FIG. 11

a wash bottle containing the same strength acid, and continue to wash with this acid until the washings come through perfectly clear. Then wash with water until the washings no longer react for hydrochloric acid when tested with silver nitrate. Dry the carbon, and filter by placing the boat in an air bath heated to about, but not above, 100°. While this is drying, weigh the absorption bulb and prolong, and place them in their proper position in the carbon train, which is shown in Fig. 11, and is prepared as follows:

The gasometers *a* and *b* contain air and oxygen, respectively, and are connected with the **Y** tube *c*, which passes through a rubber stopper in the end of the porcelain tube fitted in the combustion furnace *d*, known as the preheating furnace. This tube should project at least 5 inches at each end of the furnace to prevent the rubber stoppers from becoming hot, and contains 8 or 10 inches of granulated copper oxide. Next comes the Geissler bulb *e* containing a strong solution of potassium hydrate, and known as the *purifying bulb.*

This is connected with the combustion tube proper, placed in the combustion furnace *f*. It is a tube of royal Berlin porcelain of $\frac{5}{8}$ inch internal diameter, and glazed inside and out. If a 14-inch Bunsen furnace is used, the tube should be from 24 to 28 inches long, and should be so placed that at least 5 inches of it project at each end of the furnace. To prepare this tube, place three or four tightly fitting disks of copper gauze towards one end of it, pour about 4 inches of granulated copper oxide on to them, and hold this in place by placing three or four more disks of copper gauze against it. Next to these, place a roll of pure silver gauze (about 2 inches in length) that nearly fills the tube, and place the tube in the furnace so that the gases evolved when the carbon is burned will pass through the roll of silver and the copper oxide. To the combustion tube attach a bubble tube *g* filled to about one-half its capacity with an acid solution of ferrous sulphate, to catch any free chlorine that may escape from the combustion tube, and connect this with a second bubble tube *h* filled to nearly one-half its capacity

with silver sulphate and water, to absorb any hydrochloric acid that may be mixed with the carbon dioxide. Tightly stoppered test tubes may be made to serve for the bubble tubes.

Next attach a **U** tube *i* filled with dry granulated calcium chloride, to dry the gas. To this, attach the weighed Geissler absorption bulb *j* containing a solution of potassium hydrate, and connect this with the weighed prolong *k*, which is filled with pure granulated calcium chloride that has been dried for half an hour in a platinum or porcelain dish over a Bunsen burner. Care must be taken not to fuse the calcium chloride while drying it. Different parts of the same lot of calcium chloride should be used to fill the prolong and the tube *i*, so that their drying power will be the same, and, whenever one of these tubes is refilled, the other should also be refilled from the same lot of calcium chloride. To the prolong, attach a **U** tube *l*, also filled with calcium chloride, to prevent any moisture from entering the combustion train from this end, and attach this **U** tube to an aspirator. All connections must be perfectly tight, so that gas can neither enter, nor escape from, the apparatus, and the ends of the glass tubes should come as near as possible to meeting inside of the rubber tubing used for connections. The pressure in the gasometers *a* and *b* should be so regulated that it will force air or oxygen through the purifying bulb *c*, but will not force them through the bubble tubes *g* and *h*.

When ready to commence a combustion, light the burners of the preheating furnace *d*, and gradually increase the temperature until the combustion tube containing copper oxide is red hot for 5 or 6 inches of its length. Then place the platinum boat containing the carbon next to the roll of silver foil in the combustion tube of the furnace *f*, and close the connection. Start the combustion by lighting enough burners, under the part of the tube in the furnace *f* that contains the copper oxide, to embrace about 3 inches of it in flame. Then see that the connection between the air gasometer and the preheating furnace is closed; turn on the oxygen, and regulate the aspirator so that about three bubbles per second

pass through the bulb j. The heat and aspiration must be so regulated that a steady current of oxygen passes through the bulb c, and there must not be back pressure at this point at any time during the operation. When the tube over the burners has become fairly red, turn on two more burners, and, when the tube has become red above these, turn on the burners one at a time, allowing the tube to become red above each burner before the next one is turned on, until the tube under the boat, and for 2 or 3 inches back of it, is embraced in flame.

After the tube has become red over all the burners lighted, allow the combustion to proceed for from 20 to 40 minutes, depending on the amount of carbon to be burned. Now, turn off every second burner, stop the supply of oxygen, turn on the air, and aspirate until about 1.5 liters of air have passed through the absorption bulb j at the rate of about three bubbles per second. While the aspiration is going on, turn out additional burners as fast as possible, without danger of breaking the tube from too sudden cooling. When the required amount of air has passed through, remove the absorption bulb and prolong, cover each end with a short piece of rubber tubing, one end of which is closed, with a piece of glass rod, stand them in the balance case 15 minutes to assume the temperature of the balance, and weigh. The increase in weight is the weight of carbon dioxide CO_2 produced by the combustion of the carbon, and contains 27.27 per cent. of carbon. When 3 grams of sample are taken, the weight of carbon dioxide, divided by 11, and the result multiplied by 100, gives the percentage of carbon in the sample.

Before making a determination by this method, two blanks should be run, and if the weight of the bulb and prolong changes to any great extent, something is wrong with the apparatus or chemicals. When two blanks are run without changing the weight of the absorption bulb and prolong more than 1 milligram, the last weight obtained in running the blank may be taken as the first weight in making a determination.

Dr. C. B. Dudley, to whom we are indebted for this

method, advises the use of a small absorption bulb and prolong, the whole, when filled and ready for use, to weigh from 50 to 60 grams.

2. *Combustion by Chromic Acid.*—Pour the solution in which the carbon is suspended through a felt of pure ignited asbestos in a filtering tube, prepared as shown in Fig. 5, leaving as much as possible of the carbon in the vessel in which solution was accomplished. To the carbon in this vessel, add 10 cubic centimeters of hydrochloric acid of 1.1 Sp. Gr. and so manipulate that the acid shall touch every part of the vessel that has come in contact with the solvent liquid. Pour this through the filter, wash the carbon on to the asbestos by means of a wash bottle containing acid of the same strength, and continue to wash with this acid until the washings are colorless as they come through. Then wash with distilled water for some time after the washings cease to give a reaction for hydrochloric acid when tested with silver nitrate. Transfer the carbon and asbestos to the flask *a*, using not more than 20 cubic centimeters of water to rinse in the carbon, and place the flask in position in the carbon train, shown in Fig. 12.

The flask *a* containing the carbon is fitted with a doubly perforated stopper, through one perforation of which the funnel tube *b* is passed. This is connected with the **U** tube *c*, which is filled with lumps of fused potassium hydrate, and acts as a purifying tube. Through the other perforation in the stopper of the flask *a*, is passed a tube connecting with the bubble tube *d*, containing pyrogallic-acid solution to absorb free chlorine and chlorine compounds of chromium. The bubble tube *e* is filled to a little less than half its capacity with an acid solution of ferrous sulphate, and *f* is a similar bubble tube, filled to a little less than half its capacity with an acid mixture of silver sulphate and water. The **U** tube *g* is filled with pure, dry, granulated calcium chloride.

Next comes the Geissler absorption bulb *h*, containing a strong solution of potassium hydrate, and to this is attached the prolong *i*, containing pure, dry, granulated calcium chloride. The absorption bulb and prolong are weighed

before they are introduced into the train. The prolong is connected with the **U** tube *j*, containing granulated calcium chloride, to prevent the entrance of moisture at the end of the train, and this is connected with an aspirator. A weighing **U** tube, filled to two-thirds its capacity with soda

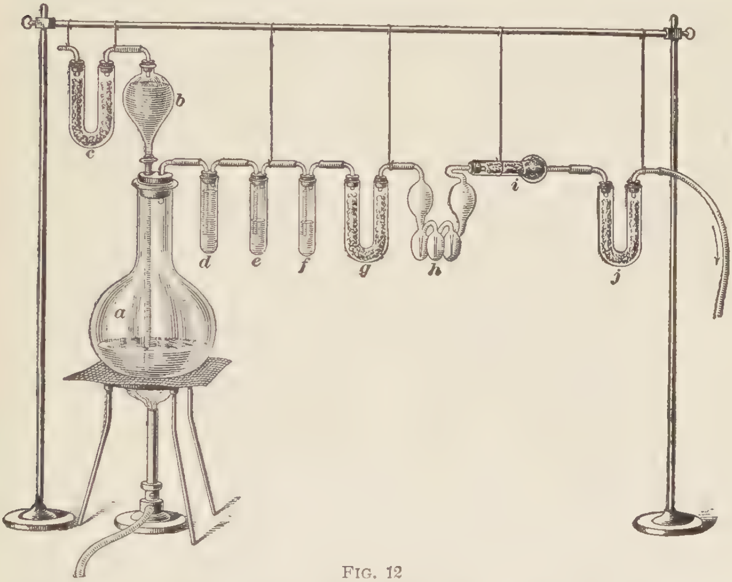

FIG. 12

lime and the other one-third with granulated calcium chloride, is sometimes substituted for the absorption bulb and prolong, but this change is not to be recommended. In making connections, bring the ends of the glass tubes as near together as possible, under the rubber tubing, and be sure all connections are perfectly tight before commencing a determination.

When all is in readiness, remove the stopper from the separatory funnel *b*, introduce 10 cubic centimeters of a saturated solution of chromic anhydride CrO_3, allow it to flow into the flask *a* containing the carbon, and close the stop-cock. Now pour 100 cubic centimeters of concentrate sulphuric acid that has been heated nearly to boiling with a little chromic anhydride, into the separatory funnel, insert

the stopper carrying the purifying tube *c*, and, by turning the stop-cock, allow the acid to pass slowly into the flask *a*. Use the aspirator if necessary. Do not, under any circumstances, allow any gas to pass out through the separatory funnel. Keep air passing through the apparatus so that about three or four bubbles per second show in the absorption bulb. After a few moments, bring a burner, turned very low, under the flask *a*, and gradually increase the temperature until the acid mixture just begins to boil, and maintain this temperature for 10 or 15 minutes.

The carbon will now all be converted into carbon dioxide CO_2 by the oxidizing mixture. Gradually lower the flame of the burner, and, finally, turn it out, keeping the current of air through the apparatus constant, however. When about 1 liter of air has passed through the absorption bulb after the light is extinguished, disconnect the absorption bulb and prolong; cover each end with a short piece of rubber tubing, the other end of which is closed with a piece of glass rod, stand them in the balance case 15 minutes to assume the temperature of the balance, and weigh. The increase in weight is the weight of carbon dioxide CO_2 from the combustion of the carbon, and contains 27.27 per cent. of carbon. When 3 grams of sample are taken, the percentage of carbon may be calculated by dividing the weight of carbon dioxide by 11, and multiplying the result by 100.

This method is not generally considered as reliable as the first one, but the apparatus is simpler and less expensive, and when carefully performed by a skilled analyst, it yields very accurate results.

3. *Combustion in Platinum Crucible.*—This method was originated by Dr. W. P. Shimer, and the description of the method and apparatus employed is mainly taken from the Journal of the American Chemical Society, and the catalogue of the Baker and Adamson Chemical Company, who control the patents on the Shimer apparatus.

At first the special water-cooled stopper was used with an ordinary platinum crucible, the upper part being cooled by a wet wick wrapped around it. The special water-jacketed

crucible, while increasing the cost of the apparatus, is a decided improvement.

The Shimer combustion apparatus comprises a special platinum crucible, provided with a copper, brass, or silver stopper and rubber-band seal. The upper edge of the platinum crucible is bent outwards and back upon itself, forming a cooling chamber about $\frac{1}{8}$ inch wide and $\frac{1}{2}$ inch deep. Short platinum inlet and outlet tubes are attached to opposite points of this chamber for the ingress and egress of a cooling stream of water. The copper stopper is hollow and provided with inlet and outlet tubes for the circulation of cooling water within its walls, and for the entrance and exit of gases to and from the interior of the crucible. The side wall of the stopper is tapered, and slightly smaller in diameter at its base than the opening in the crucible, the space between the two being filled and made gas-tight by means of a rubber gasket or band stretched around the base of the stopper. The circulation of cooling water within the stopper and the water-jacket surrounding the upper edge of the crucible permits the lower part of the crucible to be heated to the full temperature of the blast lamp without in the least affecting the rubber band, or the security of the seal. The construction and arrangement of the several parts of the apparatus are clearly shown in Figs. 13 and 14. *a* and *b* are the inlet and outlet tubes

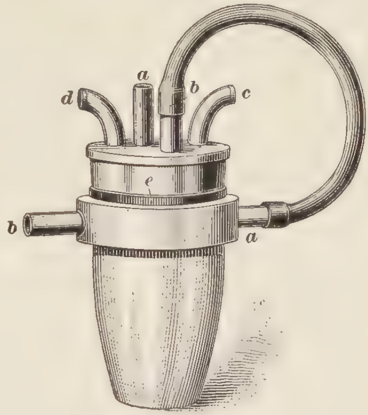

Fig. 13

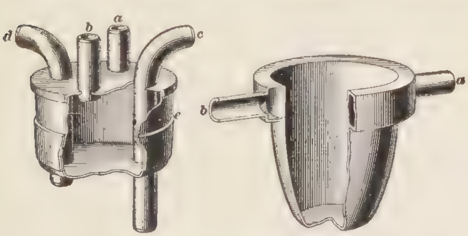

Fig. 14

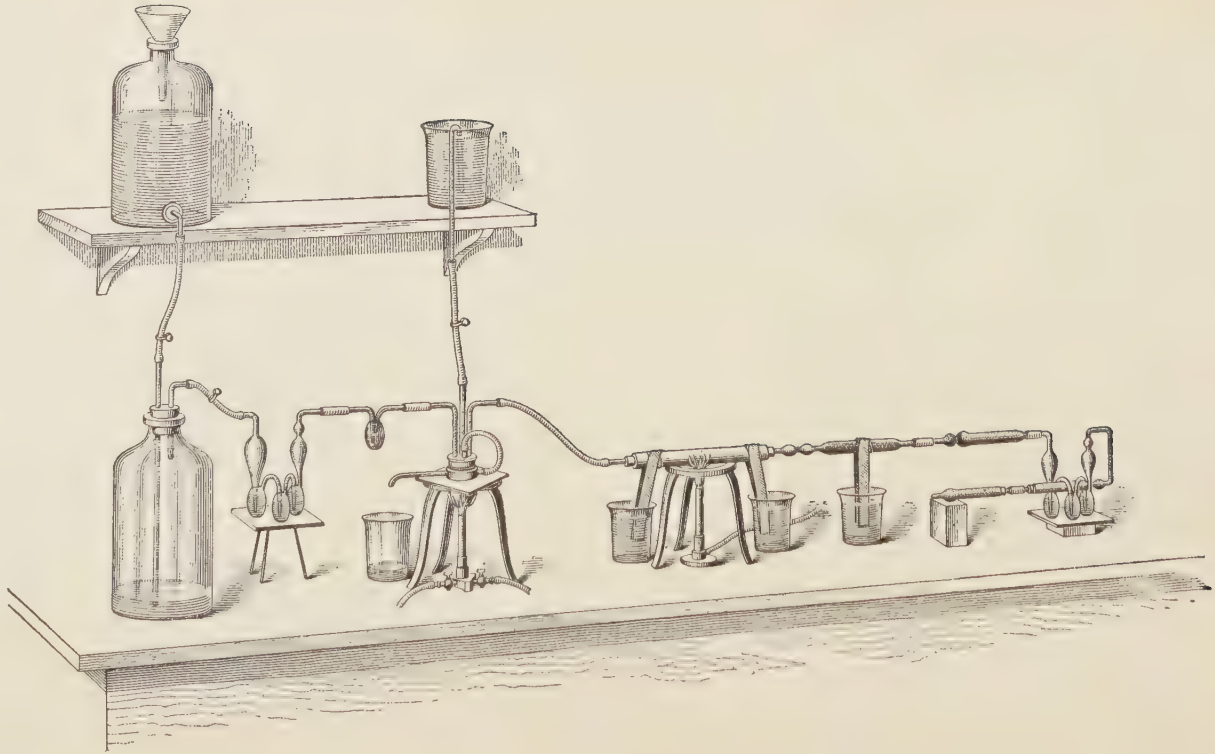

FIG. 15

for the circulation of cooling water; *c* and *d* are, respectively, the inlet and outlet tubes for the transmission of the air and the products of oxidation; *e* is the rubber gasket or band of pure black rubber, such as can be obtained from stationers.

Fig. 15 shows the complete apparatus for the combustion. It consists of the following parts, beginning at the left:

1. Two aspirator bottles, the upper filled with distilled water and the tube leading to the lower bottle extending to the bottom of the latter.

2. Potassium-hydroxide bulbs containing potassium hydroxide of 1.27 specific gravity.

3. A little guard bottle to retain any drops of potassium hydroxide that may be forced over from the Geissler bulbs.

4. The combustion crucible connected with its reservoir of water for supplying the stopper; the piece of stout asbestos board perforated to support the crucible at a point about half-way through. Under the crucible is placed the blast lamp.

5. Next to the crucible is the cupric-oxide tube, a short brass tube, 10 to 12 inches long, of small diameter, filled in its middle portion with cupric oxide. The ends of this tube are kept cool by pieces of wick wrapped around them; the wick is kept wet by having the ends dip in beakers of water. The brass tube is filed down at the ends and the rubber tubing is stretched over them. The tube is supported across the top of a tripod, with a single good Bunsen burner with flared top below, to heat to a red heat $1\frac{1}{2}$ to 2 inches of the cupric oxide. A piece of stout asbestos board is laid across the top of the tripod to retain the heat.

6. Next to the cupric-oxide tube is a glass tube filled with glass beads, wet with water, and kept quite cold externally by wet wick, to retain chlorine and hydrochloric acid. The wick is wrapped about the tube, the free ends hanging in a beaker of distilled water.

7. A large calcium-chloride tube.

8. The potassium-hydroxide bulbs or soda-lime tube.

9. A guard tube of calcium chloride.

From 2 to 3 grams of drillings are treated with double chloride of copper and potassium as previously directed.

The carbon is filtered upon asbestos in the following manner: A glass rod about 1 inch longer than the stem of the funnel (an ordinary funnel, $2\frac{1}{2}$ inches in diameter) and small enough in diameter to pass easily through the stem, is flattened out at one end and notched at two or three places by pressing the red-hot glass against the sharp corner of a file.

In preparing the filter, very short-fibered ignited asbestos is used, with fibers not longer than $\frac{1}{16}$ inch. This is well stirred with distilled water so as to have it well in suspension in a rather large bulk of water. A small piece of dry asbestos about the size of a pea is placed in the bottom of the funnel upon the end of the glass rod; this is to prevent the finely divided and suspended asbestos from packing into the passage, thus impeding filtration. The suction is now turned on and a little of the suspended asbestos is poured on. When this has been deposited as a fine horizontal felt, pour on more asbestos. If the asbestos fibers are short enough, a perfectly tight filter may be made with not more than $\frac{1}{4}$ inch of asbestos. A small bulk of filter greatly facilitates subsequent transference and combustion. When dry, the carbon may usually be picked off in a thin shell by means of a pair of forceps; it is easily transferred to the empty crucible with the carbon side down. It is well to have a circular piece of thin platinum foil in the bottom of the crucible. The small amount of carbon remaining in the funnel is removed by use of a little ignited asbestos. It is necessary to be careful to keep all the carbon within about $\frac{1}{4}$ inch from the bottom of the crucible, which is not at all difficult to do. If a part of the carbon were to be $\frac{1}{2}$ to $\frac{3}{4}$ inch from the bottom, it might escape complete combustion. Graphitic carbon from pig iron is easily burned in air at the white heat attainable by the blast lamp. After the carbon is all transferred, a little ignited asbestos is filled in on top of it.

Another way is to add a little finely divided, ignited asbestos to the solution, and to filter the carbon on a Gooch crucible. The Gooch, without its cap, is then placed on the

bottom of the combustion crucible. This method has the advantage of rapid filtration, quick transference, and avoidance of contact of the carbon and traces of copper oxide with the bottom of the combustion crucible. A Gooch crucible may be made out of an old ignition crucible.

While the funnel containing the carbon, after being washed, is drying, connect up the apparatus and test it as follows: Fill the crucible one-third full of ignited asbestos and close it, first wetting the rubber band. A little wet wick wrapped several times about each end of the brass cupric-oxide tube inside of the rubber connections and hanging in beakers of water, will avoid all risk of burning. The moisture tube is disconnected and filled with cold distilled water, and the excess is allowed to drain out by holding the tube in a vertical position. Open the clamp and allow water to run through the stopper. Now put the Bunsen flames under the crucible and the middle of the cupric-oxide tube, covering the latter with a piece of asbestos board. Open the clamp between the upper and lower aspirator bottles and leave it fully open. Open the clamp between the lower aspirator bottle and the potassium-hydroxide bulb and regulate the passage of air by this clamp alone. Let air bubble through the apparatus, at the rate of 3 bubbles per second, for 20 minutes. Detach and weigh absorption apparatus with the usual precautions. A second weight nearly always agrees well with the first. When the constant weight is obtained, the carbon is transferred to the crucible as described and the combustion is begun, after, of course, testing the apparatus for tightness. Before putting the stopper into the crucible it is best to wet the rubber band with the wet finger. This prevents friction and insures a tight crucible. Be sure that water is running from the stopper and that the cupric-oxide tube is red hot for from $1\frac{1}{2}$ to 2 inches, then turn on the air at the speed of about 3 bubbles per second and bring a small blast-lamp flame immediately under the crucible so as to heat the bottom to a bright-red heat, extending at least $\frac{1}{4}$ inch from the bottom. A large flame is to be avoided. The bottom of

the crucible should be flat or, better, slightly convex—never concave. Combustion begins immediately, and in 1 or 2 minutes carbon dioxide begins to be absorbed by the potassium-hydroxide bulbs. Combustion is complete in 25 minutes or less. At the end of this time remove the blast lamp and aspirate 4 liters of air through the apparatus. Then detach and weigh the absorption apparatus with the usual precautions. The increase in weight is the CO_2, which contains 27.27 per cent. carbon. In removing the asbestos from the crucible there is often, when copper solution has been used for dissolving the sample, a black residue remaining where the carbon was, which may mislead the inexperienced, but it is oxide of copper, as is easily proved by its solubility in strong hydrochloric acid.

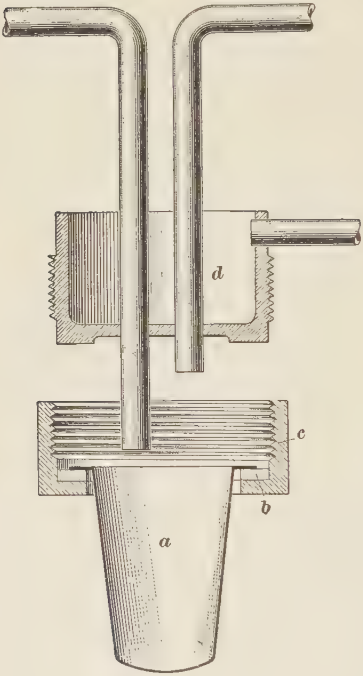

FIG. 16

When the carbon, after filtration, is well washed both with hydrochloric acid and hot water, there is very little chlorine or hydrochloric acid to fear, and the moisture tube effectually stops it. After every five or six combustions, it is only necessary to rinse out the tube with distilled water and connect it again. The tube is 6 inches long and $\frac{3}{4}$ inch in diameter. The two bulbs are empty; the tube itself is filled with glass beads of about $\frac{1}{8}$ inch in diameter; it retains about $2\frac{1}{2}$ cubic centimeters of water when drained.

This method of combustion in a platinum crucible has been largely introduced in iron and steel-works laboratories, and yields excellent results. Great care, however, must be

taken not to heat the upper part of the crucible enough to burn the rubber band. To avoid this danger and at the same time furnish a less costly piece of apparatus, John V. R. Stehman has devised the ignition crucible and water-cooled stopper shown in Fig. 16.

The crucible *a* is of platinum with a flange around the top. At *b* is shown a washer made of a piece of acid-washed, asbestos wick yarn. This is moistened, laid on the flange of casing *c*, and then pressed into place by screwing *d* down upon it, the crucible being left out. This flattens the washer and forces out the excess of moisture. The crucible is now dropped into place and *d* moved down upon it. The bottom of *d* is turned true and polished and makes an air-tight joint with the crucible and asbestos washer. Water is supplied to the cooling cup by a tube reaching to the bottom of the cup and connected with the water reservoir. This tube is not shown in the figure. This crucible may be substituted for Shimer's model and the determination carried out as just described.

57. Graphite.—There are two methods for the determination of graphite in steel and pig iron that are more or less used, and both are here given. The first method, according to which the sample is dissolved in hydrochloric acid, is the most largely used, but the second method, in which the sample is dissolved by nitric acid, yields the most uniform, and probably the most accurate, results. The details of the two methods are as follows:

1. *Solution in Hydrochloric Acid.*—Dissolve 1 gram of pig iron, or from 5 to 10 grams of steel, in hydrochloric acid of 1.1 Sp. Gr., using 25 cubic centimeters of the pig iron, or 15 cubic centimeters for each gram of steel taken. Cover the beaker, and boil for 10 or 15 minutes. Filter on an asbestos felt in a platinum boat or filtering tube, washing the carbon on to the asbestos with a jet of hot water. Wash alternately on the felt with hot water and hydrochloric acid of 1.1 Sp. Gr., and then wash two or three times with hot water to remove the hydrochloric acid. Now wash the

precipitate with a solution of potassium hydrate of 1.1 Sp. Gr. until all effervescence, due to silicon, ceases; wash the potassium hydrate out of felt with hot water, then wash twice with alcohol and twice with ether, and, finally, wash with hot water until the last trace of ether is removed from the precipitate and filter. If a direct combustion method is to be used, dry it at a temperature slightly below 100°, introduce it in a combustion tube or crucible, and burn it in oxygen or air, following the directions previously given. If combustion by chromic acid is used, transfer the asbestos and carbon to a flask, using not more than 20 cubic centimeters of water to wash it in, and oxidize the carbon by means of chromic anhydride and sulphuric acid, following the directions given in Art. **56,** 2. In either case, the increase in weight of the absorption bulb and prolong is the weight of carbon dioxide obtained. From this, calculate the percentage of carbon, and call the result *graphite*.

2. *Solution in Nitric Acid.*—Weigh 1 gram of pig iron, or from 5 to 10 grams of steel, into a beaker, and dissolve in nitric acid of 1.2 Sp. Gr., using 25 cubic centimeters for the pig iron, or 15 cubic centimeters for each gram of steel taken. Stand aside until the residue settles, filter on a felt of ignited asbestos in a platinum boat or a filtering tube, washing the carbon on to the asbestos with hot water, and wash thoroughly on the filter with hot water. Then wash the residue with a solution of potassium hydrate of 1.1 Sp. Gr., follow this treatment by washing several times, alternately, with hot water and hydrochloric acid of 1.1 Sp. Gr., finally washing the acid out of the filter with hot water. Next wash twice with alcohol, then twice with ether, and, finally, wash thoroughly with hot water. If direct combustion is to be used, dry it at a temperature slightly below 100°, place it in a combustion tube or crucible, and burn in oxygen or air as previously directed. If combustion by chromic acid is used, transfer the asbestos to a flask, using less than 20 cubic centimeters of water to rinse the carbon in, and oxidize by means of chromic anhydride and sulphuric acid, following the directions given in Art. **56,** 2. In either case, calculate

the percentage of carbon found from the weight of carbon dioxide, shown by the increase in weight of the absorption bulb and prolong, and call the result *graphite*.

58. Combined Carbon.—Having determined the total carbon and the graphite in a sample, the combined carbon is obtained indirectly by subtracting the graphite from the total carbon. This process would be much too long for general use in a steel-works laboratory, and, for the routine work, the color method is universally employed. This method, as we have already pointed out, probably only gives a part of the combined carbon, but, as this is not certain, and as the part shown by this method is supposed to be the only part exerting any important influence on the character of the steel, the results obtained by it are at present reported as combined carbon.

59. The Color Method for Carbon.—The color method depends on the fact that when a sample of steel is dissolved in pure nitric acid of 1.2 Sp. Gr., it imparts to the solution a depth of color that is directly proportionate to the amount of combined carbon it contains. Hence, the amount of combined carbon may be determined by comparing the color of the solution of the sample to be analyzed with the color of the solution of a sample in which the carbon has been carefully determined by combustion methods. There are several things, however, that have an influence on the color produced. The method of solution, the chemical composition of the steel, the physical treatment it has received, and the process by which it was manufactured, all appear to have their influence on the color produced; hence, the standard steel should have, approximately, the same composition, should have been manufactured by the same process, and receive the same physical treatment, and should be dissolved in the same manner and at the same time as the samples to be tested. The best results are obtained when both the standard steel and the samples for analysis are taken as the metal is poured into the mold.

A number of modifications of this method have been published, and are used, and many of them have advantages for steels of certain composition. One that the writer has used very largely, and found to give excellent results with samples of any composition, is as follows:

Weigh out .5 gram of the standard steel, and exactly the same weight of each of the samples for analysis; transfer each to a properly labeled test tube 7 inches long by $\frac{7}{8}$ inch in diameter, and stand the test tubes in a rack similar to the one shown in Fig. 17, in which *a* is a copper disk perforated to receive the test tubes, and *b*, which is joined to the copper disk by the supports, is a disk of coarse copper gauze for the test tubes to rest on.

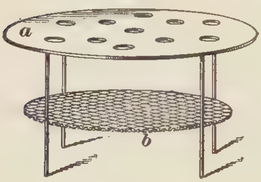

FIG. 17

Place the rack containing the test tubes with the samples in a vessel of cold water, and add 10 cubic centimeters of nitric acid of 1.2 Sp. Gr. to each. The nitric acid used for this purpose should be perfectly pure, and under no conditions must it contain chlorine or hydrochloric acid. When violent action ceases, place the rack containing the tubes in a water bath containing boiling water, and leave them in this for 5 minutes after all the steel is dissolved, shaking the tubes occasionally, if necessary, to prevent the formation of a film of iron oxide. Stand the rack in a dish of cold water 2 minutes for the solutions to cool, decant the standard into a graduated reading tube of colorless glass, and dilute it until 1 cubic centimeter of the solution represents .01 per cent. of carbon.

Thus, if the standard contains .15 per cent. of carbon, dilute the solution to 15 cubic centimeters with distilled water. Now decant one of the samples to be tested into a similar reading tube that has exactly the same dimensions as the one containing the standard, and dilute it until its color exactly matches the standard. Each cubic centimeter of this will now represent .01 per cent. of carbon. Thus, if the solution amounts to 18 cubic centimeters, the sample

contains .18 per cent. of combined carbon. As soon as the reading is taken, this tube should be emptied, rinsed, a second sample introduced, diluted, and read in the same way.

Not more than 10 samples should be analyzed at once, and the readings should be taken as rapidly as possible, for the standard gradually loses its color when allowed to stand. The colors should be compared in diffused light. It is best to stand in front of a window facing north, when comparing them, and a piece of wet filter paper pressed against the back of the tubes sometimes helps to determine the exact tint. A camera, shown in Fig. 18, is sometimes used for this purpose. It consists of a box of light wood, blackened inside. About 1 inch from the end *b*, a piece of ground glass is inserted. Just back of this, two openings are made in the top to receive the comparison tubes. By viewing the solutions from the end *a*, the tints are determined.

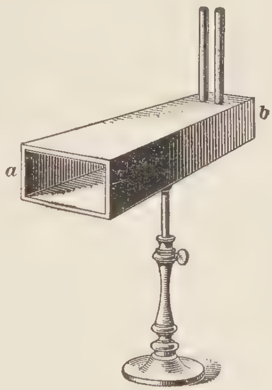

FIG. 18

If the steel contains more than .4 per cent. of combined carbon, it is best to use samples weighing .2 or .3 gram, and dissolve them in 5 or 6 cubic centimeters of nitric acid. As it takes some time, as a rule, to dissolve samples containing so much carbon, it is best to place small glass bulbs in the mouth of the tubes to prevent loss of acid by evaporation during solution. In reading such samples, dilute the standard until 1 cubic centimeter represents .02 or .03 per cent. of carbon, dilute the sample until the colors agree, and multiply the reading by the factor. For instance, let us suppose that the standard steel contains .6 per cent. of carbon, and the solution is diluted to 20 cubic centimeters. Each cubic centimeter will then represent .03 per cent. of carbon. If the solution of a sample, when diluted to match this, amounts to 22 cubic centimeters, it contains $22 \times .03 = .66$ per cent. of combined carbon.

SOLUTIONS FOR CARBON DETERMINATIONS

60. Copper Potassium Chloride.—To make the acid copper-potassium-chloride solution, used in dissolving the sample for the determination of total carbon, dissolve 1 pound of solid salt in 1,300 cubic centimeters of water, and, if the solution is not perfectly clear, filter through ignited asbestos. To the clear solution or filtrate, add 100 cubic centimeters of pure concentrate hydrochloric acid, and stir well to secure thorough mixing.

61. Potassium Hydrate.—The potassium-hydrate solution used in the absorption bulb, and in the purifying bulb, is made by dissolving pure solid potassium hydrate in a small amount of water, and diluting the solution until it has a specific gravity of 1.27 when cold. About 1 liter of this solution may be made from 400 grams of solid potassium hydrate.

62. Ferrous Sulphate.—To make the acid solution of ferrous sulphate, dissolve the pure crystallized salt in water, making almost a saturated solution, and to every 50 cubic centimeters of this solution add 5 drops of concentrate sulphuric acid. This solution is used to absorb free chlorine. It appears to form hydrochloric acid, and to retain most of the acid thus formed.

63. Silver Sulphate.—Doctor Dudley recommends the following method for the preparation of this solution: Precipitate silver carbonate by adding sodium carbonate to a solution of silver nitrate. Filter and wash thoroughly. By means of a little water, transfer the precipitate to the bottle in which it is to be kept, and add sulphuric acid—at last, drop by drop—while agitating the mixture, until the carbonate is completely decomposed and the liquid is distinctly acid to test paper. To fill the bubble tube, shake the bottle well and pour enough of the milky mixture into the tube so that about $\frac{1}{4}$ inch of solid will settle to the bottom; then add water to fill the tube to nearly one-half its capacity. This

solution absorbs any hydrochloric acid that may pass over from the ferrous-sulphate tube.

64. Pyrogallic-Acid Solution.—This solution is made up by mixing .2 gram of pyrogallic acid, 5 grams of neutral potassium oxalate, and 3 grams of pure sodium chloride, and dissolving the mixture in water sufficient to make 20 cubic centimeters of solution. When dissolved, add 2 drops of concentrate sulphuric acid, which must render the solution distinctly acid to test paper. This solution absorbs free chlorine and chlorochromic acid. It may liberate hydrochloric acid, as it tends to form this acid from the oxides of chlorine.

ANALYSIS OF COAL AND COKE

PROXIMATE ANALYSIS

65. A proximate analysis of coal is nearly always required, and, although the results obtained are, to a great extent, merely comparative, yet, when the directions given are strictly followed, the results obtained are accurate enough to be of great service in determining the value of the coal for various purposes. It is of the utmost importance that the directions given should be followed exactly in every case, for slight variations in the method give large differences in the results, and as the results, so far as *moisture*, *volatile combustible matter*, and *fixed carbon* are concerned, are only comparative, they must be obtained under exactly the same conditions in every case if they are to be of any value.

In selecting a sample, about 5 pounds of the coal should be taken, exercising care, of course, to get a sample representing the whole quantity. Break this up and quarter it down until a sample weighing about 100 grams is left. Pulverize this, and keep it in a tightly stoppered bottle until analyzed. The quartering and pulverizing should be carried out as rapidly as possible, to prevent the absorption or loss

of water, and, as coal in the powdered form changes in other respects, especially when exposed to air, it should be kept in a tightly stoppered bottle, and the analysis should be made as soon as convenient after the sample is taken. A method of analysis that gives concordant results, and is probably more largely used than any other at the present time, is as follows:

66. Moisture.—When coal is dried at a temperature slightly above 100°, it loses in weight for a time, and then begins to grow heavier. Consequently, we cannot dry the sample in the ordinary way until a constant weight is obtained, and it is necessary to dry all samples for a certain time at a fixed temperature to obtain concordant results. The following method of doing this has been generally adopted: Weigh 1 gram of the pulverized sample into a porcelain or platinum crucible. Place the crucible, uncovered, in an air bath having a temperature ranging from 104° to 107°, and heat it at this temperature for exactly 1 hour. Place the crucible in a desiccator, cover it, and allow it to cool. As soon as cool, weigh covered, and call the loss in weight *moisture.*

67. Volatile Combustible Matter.—Weigh 1 gram of the pulverized sample into a clean platinum crucible, weighing 20 to 30 grams and having a tightly fitting cover. Place the cover on tight, and heat over a good Bunsen burner for exactly 7 minutes. The burner should be adjusted so that it gives a good flame 20 centimeters high. The crucible should be supported, but on a platinum triangle, so that the bottom is 7 centimeters above the top of the burner. The determination should be made in a place that is as nearly free from drafts as possible. Cool the crucible in a desiccator and weigh as soon as cool. From the loss in weight caused by this treatment, subtract the amount of moisture found, and call the remainder *volatile combustible matter.* This determination should always be made on a fresh sample of coal, and not on the sample used for the determination of moisture

68. Fixed Carbon and Ash.—After weighing the crucible for the determination of volatile combustible matter, draw the cover a little to one side, place the crucible in an inclined position on a triangle, so as to admit a plentiful supply of air, place a good Bunsen burner under it, and heat until the carbon is completely burned off. This operation is likely to prove tedious, and may be hastened by letting the crucible cool from time to time, and by stirring the contents with a stout piece of platinum wire, taking care, of course, not to lose any of the material in the crucible while stirring it up. Care must also be taken not to produce too strong a current of air in the crucible while heating it, as, in this way, particles may be carried out, and a fictitious value given to the coal or coke by the apparent increase in fixed carbon and decrease in ash. When the residue in the crucible no longer shows any unburned carbon, heat it a few minutes longer, then cool it in a desiccator and weigh. The difference between this weight and the last one is the weight of fixed carbon in the sample, and the substance remaining in the crucible is ash. The percentages of the different constituents are, of course, calculated in the usual manner, and, as 1-gram samples are taken, the calculations are very simple. The sum of the percentages of fixed carbon and ash is approximately the percentage of coke that may be obtained from the coal.

69. Sulphur.—There are two methods in quite general use for the determination of sulphur in coal and coke. They are known as the fusion method and Eschka's method. The fusion method is the older, and, until quite recently, was used almost exclusively, but at the present time Eschka's method is much the more generally used. Both methods are given herewith.

1. *The Fusion Method.*—Weigh out 1 gram of the pulverized sample, mix it thoroughly with 9 grams of sodium carbonate and 5 grams of potassium nitrate, by grinding them together in a mortar, and transfer the mixture to a large platinum crucible. Rinse out the mortar by grinding

in it about 1 gram of sodium carbonate, and pour this on the mixture in the crucible. Cover the crucible and heat it over a Bunsen burner. A very gentle heat should be applied at first, and the temperature should be raised gradually, removing the cover from time to time to see that the fusion does not boil over. None of the fusion must be allowed to get on the outside of the crucible, or it will absorb sulphur from the burning gas and cause the analysis to yield erroneous results. For the same reason, care should be taken not to allow the gaseous products of the combustion to enter the crucible. When the contents of the crucible are in a state of quiet fusion, run the mass well up on the sides of the crucible, and allow it to cool.

Dissolve the fusion out of the crucible with hot water, wash the crucible thoroughly, boil the fusion until it is completely disintegrated, filter off the insoluble matter, and wash it thoroughly on the filter with hot water. Acidulate the filtrate with hydrochloric acid, and evaporate to dryness. Moisten the residue with a few drops of hydrochloric acid, add about 100 cubic centimeters of water, and heat to boiling. Filter, wash the filter well with hot water, dilute the filtrate to about 400 cubic centimeters, heat it to boiling, and precipitate the sulphur by adding from 10 to 20 cubic centimeters of a 10-per-cent. solution of barium chloride. Stand the solution in a warm place for the precipitated barium sulphate to settle, filter through a paper, or an asbestos felt in a Gooch crucible, ignite moderately, observing the precautions necessary in the ignition of this precipitate, cool, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur.

A blank determination should be made with each new lot of chemicals, using the same amount of each that is used in the actual determination; and the weight of barium sulphate that is obtained from the blank determination is subtracted from the weight obtained in each sulphur determination of the coal, before the percentage of sulphur in the coal or coke is calculated.

2. *Eschka's Method.*—Weigh out 1 gram of the pulverized coal or coke and mix thoroughly with 1.5 grams

of Eschka mixture (see Art. **71**) in a thin platinum dish of from 75 to 100 cubic centimeters capacity. A large crucible may be used instead of a dish. Support the dish on a triangle and heat slowly, holding the burner in the hand at first. If the gas ordinarily used contains sulphur—and all coal gas does contain this element—an alcohol lamp should be used, and not a Bunsen burner. Stir the mixture frequently with a platinum wire and keep the flame in motion, only touching the dish with the flame until strong glowing has ceased. Then gradually increase the heat until, in about 15 minutes, the bottom of the dish is at a low red heat. Keep at this temperature, stirring every few minutes with the platinum wire, until the carbon has completely burned; this will usually require about 1 hour. When the carbon is completely burned, allow the dish to cool, transfer the mass to a beaker, and rinse out the dish, using about 50 cubic centimeters of water. Add 15 cubic centimeters of a saturated solution of bromine in water, boil for 5 minutes, allow to settle, decant the clear liquid through a filter, add 30 cubic centimeters of water to the residue in the beaker, boil 5 minutes, allow to settle, decant the clear liquid through the filter, and boil the residue again for 5 minutes with 30 cubic centimeters of water. Filter through the same paper and wash until a few drops of the liquid running through the funnel gives no precipitate when acidified with nitric acid and tested with silver nitrate. The total volume of the liquid in the beaker under the filter should now be about 200 cubic centimeters. Add 2 cubic centimeters of concentrate hydrochloric acid and boil until the bromine is completely expelled. Test a drop of the liquid with litmus paper to make sure that it has an acid reaction. If not acid, add 1 or 2 drops hydrochloric acid and again boil. When all the bromine has been driven off and the liquid is slightly acid, add slowly to the solution, which should be kept at about the boiling point, 10 cubic centimeters of a 10-per-cent. solution of barium chloride. Stir constantly while adding the barium chloride, and add it slowly, not more than 1 drop a second.

Stand the beaker in a warm place for the precipitate to

settle; filter, wash throughly with hot water acidulated with a few drops of hydrochloric acid, ignite moderately, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur. The directions previously given should be followed in filtering and igniting this precipitate.

Although chemicals that are absolutely free from sulphur may be obtained for this determination in the market, a careful blank should be run with each new lot of reagents, for some so-called C. P. ("chemically pure") chemicals are not strictly as represented.

70. Phosphorus.—Weigh out 10 grams of the powdered sample in a platinum crucible, and burn off the carbon. This may be done as in the determination of fixed carbon, or, if the laboratory contains a muffle furnace, the crucible may be placed in this and the carbon allowed to burn, leaving the crucible uncovered in this case. As samples of anthracite coal and coke burn very slowly, the process is sometimes hastened by burning in oxygen. This may be done by covering the crucible with a perforated piece of platinum foil, and leading a slow current of oxygen through this perforation, in the same way that the hydrogen is led into the Rose crucible in the ignition of copper sulphide (see this determination).

When all the carbon is burned off, treat the residue with concentrate hydrochloric acid, dilute the solution with water, filter, wash thoroughly with hot water, and stand the filtrate aside. Dry the filter and residue, burn off the paper, and fuse the residue with about six times its weight of pure sodium carbonate. Dissolve the fusion in water, filter off the insoluble matter, and wash it well with hot water. Acidulate the filtrate with hydrochloric acid, and evaporate to dryness. Moisten the residue with a few drops of hydrochloric acid, add about 100 cubic centimeters of water, boil a few minutes, and filter. Wash the insoluble matter on the filter with hot water, and add this filtrate to the first one. To the combined filtrates, add a little ferric chloride that must be free from phosphorus, and render the solution

slightly alkaline with ammonia; then acidulate it with acetic acid, and boil a few minutes.

The precipitate formed will contain all the phosphorus. Filter and wash once with boiling water. Dissolve the precipitate in hydrochloric acid, and evaporate the solution to a small bulk, taking care not to allow an insoluble scale of iron oxide to form. Then add 5 cubic centimeters of concentrate nitric acid, and follow this in a few moments with 30 cubic centimeters of water. Filter into a flask and wash the filter well with a 2-per-cent. solution of nitric acid. To the solution in the flask, add 30 cubic centimeters of concentrate ammonia, and then about 1 cubic centimeter of concentrate nitric acid in excess of the amount required to dissolve the precipitate formed. Heat the solution to exactly 85°, add from 50 to 75 cubic centimeters of ammonium-molybdate solution, agitate the solution for 5 minutes, allow it to stand 15 or 20 minutes for the precipitate to settle, filter, wash, and proceed with the determination by one of the methods given in Art. **36,** *et seq.* It is best to use the gravimetric method, weighing as magnesium pyrophosphate, for this determination, and the directions given in Art. **16** should be followed. When using this method, if the percentage of phosphorus is low, it is best to allow the solution to stand about 1 hour for the yellow precipitate to settle.

REAGENTS FOR COAL ANALYSIS

71. Eschka Mixture.—Weigh out a convenient quantity of pure magnesium oxide that must be free from sulphur, and that has been previously ignited to expel all moisture; add to this half its weight of pure dry sodium carbonate, grind them together until they are thoroughly mixed, and keep the mixture in a tightly stoppered bottle. A bottle with a ground-glass stopper is preferred for this purpose; at all events, the mixture must be kept dry.

72. Calorific Value of Coal.—The determination of the heating power of coal involves the use of expensive

apparatus and delicate manipulation. Such determinations will not be treated in this Course; but we give a method of calculating the heating power of coal from its proximate analysis that, on most samples, gives results very close to the results of actual measurements made with utmost care. Several formulas for making this calculation from the results of analysis have been suggested. On the whole the most satisfactory is that of Goutal, modified by De Paepe.

Let M = percentage of volatile matter;
N = percentage of volatile matter calculated on the coal supposed to be deprived of water and ash;
P = calorific power of coal;
C = percentage of fixed carbon;
A = a coefficient which varies according to the value of N.

$$N = \frac{100M}{M + C}$$

$$P = \frac{8{,}150C + AN}{100}$$

A = 14,000 for N = 2 to 12
A = 12,000 for N = 12 to 17
A = 11,000 for N = 17 to 24
A = 10,200 for N = 24 to 30
A = 9,400 for N = 30 to 35
A = 8,000 for N = 35 to 38
A = 7,900 for N = 38 to 40
A = 7,600 for N = 40 to 50

The result here, P, gives the calories set free by the combustion of 1 kilogram of coal. This multiplied by 1.8 gives the B. T. U. liberated by the combustion of 1 pound.

LIMESTONE

73. The analysis of limestone has been described in *Quantitative Analysis*, Part 4. The determinations usually required are silica, alumina, iron, lime, and magnesia.

BLAST-FURNACE CINDER

74. Most samples of blast-furnace cinder are easily decomposed by hydrochloric acid. With samples that are exceptions to this rule the cinder must be fused with sodium carbonate before treating with hydrochloric acid.

1. *Silica.*—Weigh .5 gram of the finely powdered cinder, transfer it to a porcelain casserole, or dish, add 20 cubic centimeters of water, and stir until every particle of the sample is thoroughly wet. Add slowly, and with constant stirring, 30 cubic centimeters of hydrochloric acid (1 : 1). In most cases the sample will dissolve to a clear solution, often in a few minutes setting to a clear jelly-like mass. Add 1 cubic centimeter of nitric acid, cover with a watch glass, and heat over an Argand burner until all the water has been driven off. Allow to cool, add 3 cubic centimeters of hydrochloric acid, and again evaporate to dryness. This evaporating to dryness twice is absolutely necessary in order to thoroughly decompose the silicic acid. Cool, add 20 cubic centimeters of concentrate hydrochloric acid and 40 cubic centimeters of water. Heat to nearly the boiling point for 3 minutes, filter, wash free of chlorine, transfer the wet paper and precipitate to a platinum crucible, heat first at a low temperature and finally intensely until all the paper is burned. Cool and weigh. The weight of the precipitate multiplied by 200 gives the percentage of silica SiO_2, provided exactly .5 gram of the sample was taken.

2. *Alumina.*—The filtrate from the silica, which should be about 200 cubic centimeters in a 400-cubic-centimeter beaker, is covered with a watch glass and heated to boiling. Add a slight excess of ammonia, and continue the boiling for 2 minutes. Remove from the heat and allow to settle. Decant the clear liquid through a filter, wash the precipitate, first by decantation, and finally on the paper with hot water until free from chlorine. Transfer the precipitate and paper to a platinum crucible, heat first at a low temperature and finally intensely until the paper is burned. Cool and weigh as Al_2O_3. This precipitate will contain any iron

that might be in the cinder; but the amount of this is so small that it is generally disregarded.

3. *Lime.*—Heat the filtrate from the alumina to boiling, add 25 cubic centimeters of a saturated solution of ammonium oxalate and 10 cubic centimeters concentrate ammonia. Complete the determination of calcium oxide as described in the analysis of limestone.

4. *Magnesia.*—Treat the filtrate from the calcium oxalate for magnesia as described in the analysis of limestone.

In reporting results of a cinder analysis the percentages of insoluble silicious matter—alumina Al_2O_3, lime CaO, and magnesia MgO—are generally given.

DETERMINATIONS OCCASIONALLY REQUIRED IN ORES AND PIG IRON

75. Alumina in Iron Ores.—This determination is sometimes required and is best accomplished in the following manner: Unite the filtrates from the silica determination and evaporate or dilute to 400 cubic centimeters. To the cold solution, add ammonia until it becomes dark red, but contains no precipitate. Add 3.3 cubic centimeters of hydrochloric acid, 1.2 specific gravity, and 2 grams of sodium phosphate, which should be dissolved in water and filtered. Now add 10 grams of sodium thiosulphate dissolved in water and filtered, if necessary, and 15 cubic centimeters of acetic acid, 1.04 specific gravity, heat to boiling, boil 15 minutes, filter as rapidly as possible, wash thoroughly with hot water, dry, ignite in a porcelain crucible, and weigh as $AlPO_4$, which contains 41.85 per cent. of Al_2O_3.

76. A Rapid Method for the Approximate Determination of Graphite.—Frequently in foundries determinations of graphitic carbon are required, and while the methods referred to give the best results, quicker methods, in which the graphite is weighed directly, generally give results exact enough for practical purposes. Probably the most satisfactory method of this kind is due to Crobaugh,

and is carried out as follows: 2 grams of the iron is dissolved in a 400-cubic-centimeter beaker with 100 cubic centimeters of nitric acid of 1.135 specific gravity, heating if necessary, but keeping the volume of the liquid constant by the addition of water if there is any evaporation. When the solution is nearly complete, add 3 cubic centimeters of strong, chemically pure, hydrofluoric acid, taking care not to pour it against the glass. Give the beaker a whirling motion, and the solution will generally be complete in a few minutes. Filter, using the pump, through counterpoised filter, placing both papers in the funnel, one under the other. Transfer the graphite completely to the paper, wash four times with water, then twice with hot hydrochloric acid of 1.10 specific gravity, then with water, then twice with ammonia (1 volume of concentrate ammonia to 2 volumes of water), then twice with hydrochloric acid, and finally wash clean with water. Allow the last of the wash water to run through, remove the papers from the funnel, spread them out on a glass plate, and shift the under paper so that the lines of folding do not coincide with those of the upper paper. Dry in an air bath at exactly 100° C. Place the under paper on the balance pan on which the weights are placed and the paper with the graphite on the other pan. The difference in weight is the graphite. In case all silica is not removed by the hydrofluoric acid, the paper with the graphite may be burned and the silica left weighed and subtracted.

To get counterpoised filter: Take two best quantitative filter papers of the same size, place one in each balance pan; find out which is the heavier, and with a clean sharp pair of scissors trim the heavier paper until it just balances the other.

QUANTITATIVE ANALYSIS

(PART 6)

ANALYSIS OF CLAY

CHEMICAL ANALYSIS

1. Clay is principally a product of the decomposition of feldspathic rocks, and is essentially a mixture of the silicates of aluminum, calcium, magnesium, sodium, and potassium with silica. The silicates are hydrated, so that clay ordinarily contains from 6 to 14 per cent. of combined water, and nearly all, if not all, samples contain small quantities of iron. A mechanical analysis of clay to separate the coarse from the fine parts, and a careful examination to determine the condition in which the silica exists, as well as a number of tests of physical properties, are sometimes required; but for these the student is referred to a more exhaustive treatise on the subject, and only the chemical analysis will be given here. This is ordinarily all that is required to determine the fitness of the clay for the manufacture of bricks, or for use in metallurgical operations. Clay that is to be used for the manufacture of firebrick, or in metallurgical processes where it is exposed to great heat, should not contain much iron, potassium, or sodium, as these constituents fuse rather easily. The best clay for these purposes does not contain more than 1 per cent. of either of the alkalies, or more than 2 per cent. of iron oxide. The determinations usually made are, moisture, combined water,

silica, alumina, iron oxide, calcium oxide, magnesia, and the alkalies.

2. Determination of Moisture.—Grind from 5 to 10 grams of the clay to an exceedingly fine powder in an agate mortar, weigh it on a watch glass, transfer the watch glass with the sample to an air bath, and heat it for one hour at a temperature ranging from 100° to 105°. Remove it to a desiccator, and weigh as soon as cool. Return the watch glass with the sample to the air bath, heat it 15 minutes longer at the same temperature, cool in a desiccator, and weigh again as soon as cool. If this weight differs from the previous one, the sample must be heated again, and this must be continued until a constant weight is obtained. From the loss in weight when the sample is dried at this temperature, calculate the percentage of moisture in the sample.

As soon as the sample is weighed, transfer it to a clean dry bottle or tube, and keep it tightly stoppered, to be used for the other determinations. As the other constituents are determined in the dry sample, the moisture is not included in the regular report, but is reported as a separate item.

3. Determination of Combined Water.—Weigh 2 grams of the dried sample in a platinum crucible, and ignite it for 20 minutes with the cover on, keeping the crucible at a red heat. Cool in a desiccator and weigh as soon as cool. Ignite 5 minutes longer, cool in a desiccator, and again weigh as soon as cool. If this weight differs from the previous one, the ignition must be continued until a constant weight is obtained. From the loss in weight, calculate the percentage of combined water in the sample. This method yields accurate results with most samples, but if the clay contains much organic matter or pyrite, it cannot be used. In such cases, the water should be determined by the method described under Prehnite in a former Section.

4. Determination of Silica.—Weigh out 1 gram of the dry sample, mix it thoroughly with 10 grams of fusion mixture, consisting of equal parts of the carbonates of sodium and potassium, and introduce the mixture into a large platinum crucible. Heat this over a good Bunsen burner until it begins to cake together, and then heat over a blast lamp until it has been in a state of quiet fusion for some time. The fusion may now be removed from the crucible by quickly pouring the molten mass into a clean dry platinum dish floating on cold water. The fusion, upon striking the cold platinum, solidifies quickly and will not adhere to the dish. The small quantity of fusion remaining in the crucible can be mostly removed by hot water, and the small quantity remaining after this treatment is readily dissolved out by hydrochloric acid.

At all events, dissolve the fusion in water, acidify the solution with hydrochloric acid, evaporate to dryness, and heat at about 130° until the odor of hydrochloric acid is no longer given off. To the residue, add 15 cubic centimeters of concentrate hydrochloric acid, and heat gently to dissolve the iron; then add 50 cubic centimeters of water, heat to boiling, allow the insoluble matter to settle, and filter. Wash thoroughly on the filter with hot water, wrap the paper around the precipitate, place them in a platinum crucible, and, after burning off the paper over a Bunsen burner, ignite intensely over a blast lamp, cool in a desiccator, and weigh as silica. From this weight, calculate the percentage of silica in the sample.

5. Determination of Alumina.—Heat the filtrate from the silica to boiling, add a few drops of concentrate nitric acid, then add a slight excess of ammonia while stirring continuously, and continue to boil for a few moments, taking care that the solution remains faintly alkaline. As soon as the precipitate has settled, decant as much as possible of the clear liquid through a filter, then transfer the precipitate to the filter, and wash it thoroughly with hot water. Wrap the filter around the precipitate, place them in a

platinum crucible, and, after burning off the paper over a Bunsen burner, ignite strongly over a blast lamp, cool in a desiccator, and weigh. The precipitate now consists of the oxides of aluminum and iron, $Al_2O_3 + Fe_2O_3$. After determining the ferric oxide in the sample, deduct this from the mixed oxides, and the remainder will be alumina.

The iron may be determined by fusing the precipitate of mixed oxides with acid potassium sulphate, dissolving the fusion, reducing the iron, and titrating with permanganate, as directed in a former Section under Feldspar, or the iron may be determined in a separate portion of the sample, as directed in Art. **8.**

6. Determination of Calcium.—If the filtrate from the alumina greatly exceeds 250 cubic centimeters in volume, evaporate it to about this amount; then, to the gently boiling solution, add 5 cubic centimeters of concentrate ammonia, and a moderate excess of ammonium oxalate, continue the boiling for a few minutes, and then stand the solution in a warm place for 4 hours, to allow the precipitate to collect and settle. Slightly more ammonium oxalate than is required to convert all the calcium and magnesium into oxalates must be added, but a very large excess is to be avoided. Filter off the precipitated calcium oxalate, and wash it thoroughly with hot water to which a few drops of ammonia have been added. Wrap the precipitate in the filter, place them in a platinum crucible, and, after heating gently over the Bunsen burner, to drive off moisture and burn the paper, ignite at the full power of the blast lamp until a constant weight is obtained. It is a good plan to allow the precipitate to cool, after igniting it for 5 or 10 minutes over the blast lamp, and, when cool, to moisten it with a few drops of water; then, after heating it gently to drive off the water, ignite it again at the full power of the blast lamp for 10 minutes before weighing it the first time. When a constant weight is obtained, the precipitate is calcium oxide, and from this weight, the percentage of calcium oxide in the sample is obtained.

7. Determination of Magnesium.—Evaporate the filtrate from the calcium oxalate to about 200 or 250 cubic centimeters, cool the solution by standing the beaker in cold water, and, when cold, add an excess of sodium-ammonium phosphate, drop by drop, while stirring continuously. When all the reagent has been added, pour in a quantity of concentrate ammonia equal to about one-third the volume of the solution. Stir the solution several times after the ammonia is added, and then stand it in a cool place for 6 hours, for the precipitate to separate. Filter and wash the precipitate thoroughly with cold one-third-strength ammonia containing a little ammonium nitrate. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a weighed crucible. When this is cool, add the precipitate, ignite at the full power of the blast lamp for 10 minutes, cool in a desiccator, and weigh as magnesium pyrophosphate $Mg_2P_2O_7$. From this, calculate the percentage of magnesium oxide MgO in the sample.

8. Determination of Iron.—The iron may be determined in the precipitate of alumina and iron after it has been weighed, by fusing it, and proceeding as directed in Art. **5**, or it may be determined in a fresh sample as follows: Fuse 1 gram of the sample with mixed carbonates, dissolve the fusion in water and hydrochloric acid, and evaporate to dryness, just as in the determination of silica. Moisten the residue with hydrochloric acid, dissolve it in water, filter off the silica, and wash it well with hot water, adding a few drops of hydrochloric acid with the fourth or fifth quantity of wash water. Heat the filtrate to boiling, add a few drops of concentrate nitric acid, and, after boiling the solution a few moments longer, precipitate the iron and alumina with ammonia.

As soon as the precipitate settles, filter and wash once or twice with hot water. Dissolve the precipitate in the least necessary quantity of hydrochloric acid, reduce the iron in this solution with zinc, and titrate with potassium permanganate in the usual way. A blank must be run to determine

the amount of permanganate used up by the reagents. The difference is the amount used by the iron. From the amount of iron found in this way, calculate the percentage of ferric oxide in the sample. The ferric oxide found by this determination is deducted from the alumina and iron oxide previously determined, to obtain the percentage of alumina.

9. Determination of Alkalies.—Weigh out 1 gram of the sample, place it in an agate mortar, add 1 gram of pure ammonium chloride, and grind them together intimately; then add 7 grams of pure calcium carbonate, and grind the contents of the mortar together with the pestle until thoroughly mixed. Now introduce 1 gram of pure calcium carbonate in the bottom of a large platinum crucible, pour the mixture from the mortar on this, and cover the mixture with 1 gram more of the pure calcium carbonate. Cover the crucible, place it over a Bunsen burner, turned very low at first, but gradually increase the temperature, and, finally, heat to dull redness for an hour. Treat the contents of the crucible with hot water in a porcelain dish, breaking up any hard lumps with an agate pestle, if necessary. After boiling until the mass is completely disintegrated, filter off the insoluble matter, and wash it with hot water until a small test of the washings, collected in a test tube and acidified with nitric acid, only shows a faint cloudiness when silver nitrate is added. Evaporate the filtrate to about 75 cubic centimeters, remove it from the flame, add a few drops of pure ammonia, and then a strong solution of pure ammonium carbonate as long as a precipitate forms. Stir well and allow the precipitate to settle. Filter, receiving the filtrate in a porcelain dish, and wash with hot water rendered faintly alkaline with ammonia until the washings come through free from chlorine.

Sometimes a very little ammonium carbonate is also added to the wash water. Add a few drops of hydrochloric acid to the filtrate, evaporate to a small bulk, and transfer to a small platinum dish, washing in the last portions with a little

distilled water. Evaporate to dryness on a water bath, and, after heating gently to expel all water, increase the temperature to drive off ammonium compounds, finally heating the dish to very faint redness. When cool, dissolve the residue in a little water, add a drop or two of ammonia, then a few drops of ammonium carbonate, and heat on the water bath for a few minutes. Filter, and wash with water rendered faintly alkaline with ammonia, receiving the filtrate in a small, weighed, platinum dish. Acidulate the filtrate with a few drops of hydrochloric acid, evaporate to dryness on the water bath, then place the dish in an air bath and raise the temperature from 100° to about 140°. Remove the dish from the air bath, and heat it cautiously over a burner, to expel ammonium salts, finally heating the dish until it shows a faint red tinge. Cool in a desiccator, and weigh as soon as cool. The weight of the combined chlorides of sodium and potassium is thus obtained.

Dissolve the residue in a few cubic centimeters of water, add a nearly neutral solution of platinum chloride in sufficient quantity to convert the chlorides of sodium and potassium into the corresponding double chlorides of platinum and these metals, and have a moderate excess remaining. Place the dish on a water bath in which the water is maintained at as near the boiling point as possible, and evaporate the contents to a pasty consistency. Add 35 cubic centimeters of 80-per-cent. alcohol, and stand the dish in a warm place for an hour, stirring the contents occasionally to dissolve the double chloride of sodium and platinum. Filter on a weighed paper, wash thoroughly, but not excessively, with 80-per-cent. alcohol, dry in an air bath at 130° until a constant weight is obtained, and weigh as potassium-platinum chloride K_2PtCl_6.

From the weight of potassium-platinum chloride obtained, calculate the weight of potassium chloride, and subtract this from the weight of the mixed chlorides. The remainder is the weight of sodium chloride. Calculate the sodium and potassium to the oxides, Na_2O and K_2O, and report them as such.

EXAMINATION OF WATER

PRELIMINARY REMARKS

10. The process of analysis to be pursued in the examination of water depends on the purpose for which the water is to be used. It is most frequently analyzed to determine its fitness for drinking or culinary purposes, or as a boiler supply. As the fitness of a water for these two purposes depends on entirely different conditions, a water that would be well adapted to one purpose might be absolutely unfit for the other. The subject is therefore usually divided into the analysis of potable water, and the analysis of water for boiler supply, and this division of the subject will be observed in the present work. A chemist is occasionally called on to determine the fitness of a water for some particular manufacturing process, and, although we cannot treat every possible case, the student that masters what is given here will be able to answer all such questions for the determinations necessary, and the methods of making them will readily suggest themselves.

There are several methods of reporting the results of water analyses. The oldest method, and one that is still very largely employed, is to report the amount of each constituent in grains per gallon. This method is likely to cause confusion, as there are several gallons having different capacities. The English Imperial gallon contains 70,000 grains, and the United States gallon contains 58,318 grains. By far the most rational method of reporting results, is in parts per million, or, what is the same thing, in milligrams per liter, or to report them in parts per hundred thousand. If results are reported in parts per million, or milligrams per liter, they can readily be changed to grains per gallon, if desired, by means of a very simple calculation. One liter of

water contains 1,000,000 milligrams, and one U. S. gallon contains 58,318 grains. Hence, the number of milligrams in a liter of a constituent, multiplied by 58,318, and the result divided by 1,000,000, gives the number of grains of that constituent in a U. S. gallon of the water. If this method of reporting results is adopted, it should always be stated in the report that the U. S. gallon is used.

POTABLE WATER

11. The principal determinations usually made to determine the fitness of a water for drinking and cooking purposes are: chlorine; free and albuminoid ammonia; oxygen consumed in the moist combustion process; and nitrates, nitrites, and poisonous metals. In addition to these, the total solids and the hardness are frequently determined.

It is difficult to say how much of any one of these constituents may be found in a water without condemning it, but each furnishes valuable indications, and, taken together, give a fairly good idea of the purity of the water. Obviously, impurities coming from some sources are much more injurious than if coming from others. Thus, the organic matter coming from sewage would be more injurious than the same quantity coming from vegetable matter, and, in giving an opinion as to the quality of a water, a chemist must use his judgment. If possible, the chemist should select the sample himself, in order that he may examine the surroundings, and see from what sources pollution may come. In many cases, this will aid him materially in forming an opinion in regard to the quality of the water, for, if the water is found to contain a small amount of impurity, he will know whether it is likely to be dangerous or not.

12. Collecting a Sample.—The amount of water to be collected as a sample will depend on circumstances, but in no case should less than about 2.5 liters be taken. It is best to collect and preserve the sample in a large glass-stoppered bottle. A 5-liter bottle with a ground-glass stopper

is very handy for this purpose, but in the absence of such a bottle, a large bottle, or demijohn, with a new, clean cork stopper may be used. Too great stress cannot be laid on the fact that in collecting samples and analyzing the water, strict cleanliness is absolutely essential. The reason will be obvious when the student considers that in most cases only fractions of 1 part in a million are sought. The best method of preparing the bottle for the reception of the sample is to pour in a little strong sulphuric acid, and cause it to flow over the entire inner surface of the bottle, then pour most of it out, and wash the bottle with pure water, continuing to rinse it for some time after the washings have ceased to show a trace of the acid. Then, before collecting the sample, the bottle should be thoroughly rinsed out with some of the same water that is to be analyzed. Then fill the bottle completely and empty it. This is to drive out any gaseous substances that may remain in a bottle.

In taking a sample from a river or pond, care should be taken to avoid scum or other matter floating on the surface. The bottle should be immersed at some distance from the shore, and held under the water until entirely full. A sample of river water should be taken near the middle of the stream. In examining a city supply, it is best to draw the sample from the street mains, and, in examining the water supplied to a house, the water is drawn from a faucet, in the usual manner. To obtain a fair sample in such cases, the water should be allowed to run a short time before taking the sample, in order to avoid collecting the water that has been standing in the pipes for some time.

In any case, the bottle should be nearly, but not quite, filled with the water; the stopper should be inserted at once, and a piece of clean linen cloth drawn over it tightly and tied in place. Never use sealing wax over the stopper. If it is desired to seal the bottle, seal the ends of the string that holds the cloth. The sample should be kept in a cool dark place, and the examination should take place as soon as convenient after the sample is taken. At all events, the analysis should be made within 48 hours if possible.

TOTAL SOLIDS

13. The total amount of solid matter in a sample of water was at one time considered a very important indication of its quality, but, at present, it is not regarded as very important, and is frequently omitted. As the determination is very simple, and indications of greater or less value are obtained in this way, it should usually be made. The details of the process are as follows:

14. Determination of Total Solids.—Make a water bath by filling a rather tall beaker to about half its capacity with distilled water, placing it on a gauze over a Bunsen burner, and heating it to boiling. On this, place a perfectly clean platinum dish of convenient size to be weighed (one weighing about 50 grams is a good size), and heat it for a few minutes. Remove it from the water bath, wipe the water from the outside of the dish with a clean dry cloth, heat it in an air bath at exactly 105° for 10 minutes, transfer to a desiccator, and weigh as soon as cool.

After weighing the dish, place it on the water bath again, and pour into it 100 cubic centimeters of the water to be analyzed. As a rule, the dish employed will not hold this amount, and the water must be added in successive portions. In this case, measure out 100 cubic centimeters of the water, add enough of it to fill the dish to about three-fourths its capacity, and stand the rest aside, keeping it covered to protect it from dust. When about two-thirds of the water in the dish has evaporated, add the remainder, and evaporate to dryness. Leave the dish on the bath 10 or 15 minutes after the residue appears dry, to expel the last traces of moisture; then remove it, wipe the outside with a clean soft cloth, transfer to the air bath, and keep at exactly 105° for 30 minutes; place it in a desiccator, and weigh as soon as cool. As 100 cubic centimeters (.1 liter) of the water was taken for this determination, the weight in milligrams of the residue multiplied by 10 gives the milligrams of total solids in a liter of the water, or, what is the same thing, the parts per million.

Many chemists prefer to stand the dish on a cold, clean porcelain slab to cool, but as the residues from many samples of water contain deliquescent substances, and, therefore, rapidly increase in weight when allowed to stand in the air, it is always best to cool the dish in a desiccator; and, in every case, the dish should be weighed quickly, as soon as it is cold.

15. Examination of the Residue.—Formerly, it was the custom to ignite the residue, weigh again, and call the loss *organic matter*, and the results thus obtained were considered very significant. It is now known that the loss in weight during this operation is, in most cases, principally due to other constituents, and the results thus obtained are utterly valueless as far as their original purpose is concerned. Having the solid residue, however, it is well to make a slight examination of it as follows:

Remove a portion of it to another dish, and add a few drops of hydrochloric acid. If effervescence occurs, it shows the presence of a carbonate, probably of calcium. Pour the solution into a test tube, render it alkaline with ammonia, and see if it remains clear. Then add a few drops of ammonium oxalate, and heat the solution. The formation of a white precipitate shows the presence of calcium, which, taken together with the effervescence, proves that the water contains calcium carbonate, which is found in all the water in limestone districts, and is comparatively harmless.

Cautiously heat the dish containing the remainder of the residue over a Bunsen burner, and note any change in the appearance of the residue, and any odor that may be given off. The heat should be applied very gently at first, and the temperature raised gradually, until the dish becomes red. If the residue becomes dark-colored, organic matter is indicated, and the amount of organic matter present may be roughly surmised from the depth of the color developed. Organic matter, as a rule, also emits an odor when burned, and this should be noted.

The amount of solid matter permissible in a water to be used for domestic purposes depends, of course, on the

character of the solids; hence, this determination taken alone is of but little value in determining the quality of a water. If, however, the residue is examined as directed, something more of the character of the water is indicated, and, when the results of this determination are considered together with those of the other determinations to be made, they help to form an opinion as to the quality of the water. The water may contain considerable mineral matter of a harmless nature and still be a very good water for domestic use. Many very good drinking waters contain as much as 300 or 400 milligrams of total solids per liter, and, unless the sample contains more than 500 milligrams of solid matter, it should not be condemned for domestic use for this reason alone.

CHLORINE

16. Determination of Chlorine.—In determining the chlorine in water, we avail ourselves of the well known relation between silver, chlorine, and chromic acid. When a solution of silver is added to a solution containing both a chloride and a chromate, the silver unites with the chlorine until it is all precipitated as white silver chloride, and then begins to unite with the chromic acid, forming red silver chromate. The details of the process are as follows:

Measure 100 cubic centimeters of the water into a clean porcelain dish, add a few drops of potassium-chromate solution, and titrate with a standard solution of silver nitrate. As each drop of the silver solution falls into the water, it produces a red color at the point of contact, owing to the fact that all the chlorine in this part of the water is precipitated, and the silver left over unites with chromic acid, forming red silver chromate. On stirring, this precipitate comes in contact with more chlorine, which immediately takes the silver from the chromic acid, and forms white silver chloride, thus destroying the color. This goes on until all the chlorine is precipitated as silver chloride, when an additional drop of silver nitrate will give the solution a permanent reddish color, showing that the reaction is complete. From the

quantity of silver solution used, calculate the amount of chlorine in 100 cubic centimeters of the water. This result multiplied by 10 gives the amount of chlorine in a liter. This amount of chlorine in milligrams is, of course, parts per million.

Some chemists prefer to evaporate 1 liter of the water to a small bulk before titrating, and this is a good plan, in order to check the results, when the water only contains a very little chlorine. It is also a good plan to add more of the potassium-chromate indicator, and then another drop of the silver solution, after the reaction is complete, to see if a marked increase in the red color occurs. Neither of these checks can be considered essential, however, for the writer has repeatedly checked analyses without obtaining results that differed appreciably.

17. Significance of Chlorine.—Chlorine generally exists in water combined with sodium in the form of common salt, and, as this is an article that we require, and take into the system daily, it matters little whether it is taken with our food or in the water we drink; hence, chlorine in itself, unless the amount is excessive, is no cause for rejecting a water for domestic use. Probably too much stress has been laid on the determination of chlorine in drinking water; and water that was organically pure, and of very good quality for domestic use, has been rejected on account of the chlorine it contained. This is an important determination, however, when the results are considered in connection with those obtained in the other determinations, and are intelligently interpreted. A little consideration of the matter will show how they may be of use. The water in regions remote from salt deposits frequently contains but a mere trace of chlorine, while sewage is always heavily charged with this element; hence, any considerable quantity of chlorine in a water has come to be regarded as an indication of sewage contamination.

A water containing a marked increase in chlorine over the amount usually found in the locality from which the water

comes, should certainly be regarded with suspicion. This determination is important in the examination of samples of water suspected of sewage contamination during an epidemic, on account of the rapidity with which results may be obtained. In such cases, if a water is found to contain a considerable quantity of chlorine, its use should be suspended at once, pending a further examination. It must always be borne in mind that a water may be heavily charged with organic matter of vegetable origin, and still contain but very little chlorine, and, consequently, freedom from chlorine is no sign that water is free from organic matter of vegetable origin, and this is, of course, to be avoided. Sewage contamination is regarded as more dangerous than the same amount of vegetable matter, and the amount of chlorine in a water may help us to decide whether the contamination is of animal or vegetable origin, and may thus help us to discover the source of pollution.

It is impossible to say how much chlorine a water may contain without being suspected of sewage contamination, for the normal quantity of chlorine varies greatly in different sections of the country; but when the normal quantity in any locality has been established, any increase over this amount should be regarded with suspicion. The writer has analyzed samples of water containing less than 1 part per million of chlorine, while near the coast or in the vicinity of salt deposits, water that is perfectly wholesome may contain more than 20 parts per million of this element.

SOLUTIONS FOR CHLORINE DETERMINATION

18. Silver Nitrate.—The silver-nitrate solution for this purpose is usually made of such strength that 1 cubic centimeter of it will precipitate exactly 1 milligram of chlorine. It is made up as follows: Weigh out exactly 4.79 grams of the pure, dry silver-nitrate crystals; transfer this to a graduated liter flask, dissolve it in pure distilled water, and dilute the solution to exactly 1 liter. As silver nitrate is weighable, this solution will be of such strength that 1 cubic

centimeter of it will precipitate exactly 1 milligram of chlorine, if the pure salt is used, but it is best to check it by running it against a sodium-chloride solution of known strength. To make this solution, dissolve 1.65 grams of pure, dry sodium chloride in water, dilute to 1 liter, and mix thoroughly, using distilled water that is free from chlorine, of course. Each cubic centimeter of this solution contains exactly 1 milligram of chlorine, and, therefore, should exactly match the silver solution. This solution is sometimes handy in making the determinations. After taking the burette reading when titrating, a few more drops of the silver solution may be added, to produce a deep-red color; this may be destroyed with a measured quantity of the salt solution, and silver nitrate again added until the reaction is complete. Then, by subtracting the amount of sodium chloride added from the total quantity of silver nitrate used, a check on the determination is obtained.

19. Potassium Chromate.—The solution of potassium chromate used as indicator is usually a cold saturated solution of the pure salt in pure water. The solution may be made up by dissolving about 20 grams of the pure salt in 100 cubic centimeters of water. Both the potassium chromate and the water used in making up this solution must be absolutely free from chlorine. Of course, this applies with equal force to the materials used in making up the other solutions for this determination.

THE AMMONIA PROCESS

20. The determination of total solids and chlorine gives us indications that are valuable in throwing light on the subject when considered in connection with other results, but are of little value in themselves. We now come to the determination of organic matter, and the results obtained are usually sufficient in themselves to establish the character of the water. The ammonia process is divided into two parts, the determination of *free ammonia* and of *albuminoid*

ammonia. The process depends on the fact that when a sample of water is boiled with sodium carbonate, the free ammonia (which term includes ammonium salts) dissolved in it is expelled, and passes off with the first part of the water as it is evaporated. Now, having the water free of uncombined ammonia and ammonium salts, if potassium permanganate and a large excess of potassium hydrate are added and the boiling continued, the nitrogenous organic matter is decomposed, yielding a quantity of ammonia proportional to the amount of such matter contained in the water. The ammonia is collected in the distillate, and its quantity determined by means of the very delicate Nessler reagent. The determination of the ammonia is one of the most important, if not the most important, of the determinations made in the examination of water for domestic use. The details of the process are as follows:

21. Free Ammonia.—Choose a tubulated retort that will hold from 1.5 to 2 liters, and provided with a ground-glass stopper; cleanse it thoroughly by rinsing it out, first

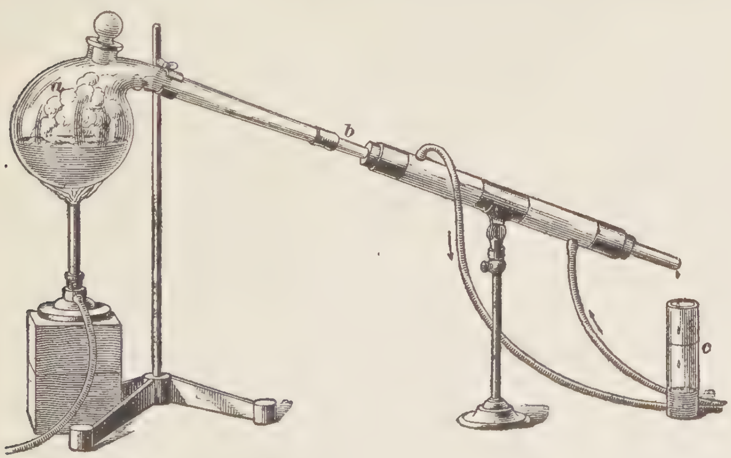

FIG. 1

with strong sulphuric acid, and then washing until the washings contain no acid, finally with distilled water, and fix it in the clamp on a retort stand, as shown at *a*, Fig. 1. Fit

the neck of the retort into the tube of a Liebig condenser, wind it tightly with a piece of thin flexible rubber, and bind this in place by means of a cord, as shown at *b*, thus securing a perfectly tight connection. Under the end of the condenser tube, stand the Nessler cylinder *c* to collect the distillate. From half a dozen to a dozen Nessler tubes will be required for the determination. They should be made of thin colorless glass, and must be of uniform size and form. Cylinders of a little more than 100 cubic centimeters capacity are probably the most convenient; each should have a mark on the side to show when 50 cubic centimeters of distillate have been collected, and they should be so nearly of the same size that these marks will all come within one-sixteenth of an inch of one another. The bottoms of the tubes should be perfectly flat, so that they will stand firmly on the working bench or table. The arrangement of the apparatus will be understood from Fig. 1.

When all is in readiness, measure 200 cubic centimeters of absolute water into the retort, add 10 cubic centimeters of sodium-carbonate solution, drop in five or six small glass balls, to prevent bumping, and close the retort with the ground-glass stopper, which must be scrupulously clean. Place a good Bunsen burner under the retort, so that the flame plays directly on it, but take care not to allow the flame to strike the glass above the water line. When 50 cubic centimeters of distillate have passed over, remove the Nessler cylinder, and place a clean one in its place, to collect the next 50 cubic centimeters of distillate passing over. When 100 cubic centimeters have passed over, remove the light from the retort. This will remove any ammonia that remained in the retort, or that may have been introduced with the sodium carbonate, and the 100 cubic centimeters of water and sodium carbonate, as well as the retort itself, are now perfectly free from ammonia. It is well to test the two distillates collected, with Nessler reagent, to learn if there was any ammonia to start with.

Now measure 500 cubic centimeters of the water to be examined into the retort, stopper it tightly, return the

burner to its position, and so regulate the flame that about 50 cubic centimeters of distillate will collect every 15 minutes. If the distillation is carried on much more rapidly than this, some ammonia will escape. While the first 50 cubic centimeters of distillate are collecting, measure different quantities of standard ammonia solution into several Nessler cylinders, and dilute each to 50 cubic centimeters with absolute water. It is handy to have such standards ranging from .005 to .05 milligram of ammonia in the 50 cubic centimeters of water. When the first cylinder is filled to the 50-cubic-centimeter mark, remove it, and stand a clean cylinder in its place, to collect the next 50 cubic centimeters of distillate passing over. By means of a 2-cubic-centimeter pipette, drop exactly 2 cubic centimeters of Nessler reagent into each of the standards and the 50 cubic centimeters of distillate, and stir each up. Allow the tubes to stand 5 minutes after adding the Nessler reagent and stirring. The reddish-brown color will by this time be developed and is fairly constant, so that one set of standards may be used for a series of determinations. The standards are made up only once a day. Have the cylinders standing on a white surface, and, by looking down through them, compare the colors and match the sample with a standard. If the sample has a color differing from that of any of the standards, a very close estimate of the amount of ammonia it contains may be made. In this case, quickly make up two more standards containing very nearly the estimated amount of ammonia, add 2 cubic centimeters of Nessler reagent to each, and, after allowing them to stand about 5 minutes, compare the sample with these standards.

When a standard is obtained, the color of which exactly matches that of the distillate, we know that each contains the same quantity of ammonia, and as the amount of ammonia in the standard is known, we thus learn the quantity in the distillate. If the distillate contains more ammonia than any of the standards, it may be diluted to 100 cubic centimeters, stirred well, half of the solution poured out, 1 cubic centimeter of Nessler

reagent added to the portion remaining in the tube to make the quantity of Nessler reagent in each tube the same, and the colors again compared. But under no circumstances must ammonia be added to a solution after the Nessler reagent has been added, for this is almost certain to give erroneous results. The free ammonia will frequently all pass over in the first three portions of distillate, and it is very seldom that any remains after the fourth, but, for the sake of uniformity, five portions of distillate, of 50 cubic centimeters each, should always be collected and Nesslerized, just as was done with the first portion. By adding the results obtained in Nesslerizing the five portions of distillate, the amount of free ammonia in 500 cubic centimeters of the water is obtained, and the result thus obtained in milligrams, multiplied by 2, gives the number of parts of free ammonia in a million parts of water.

22. Albuminoid Ammonia.—The free and the albuminoid ammonia are determined in the same sample. When 250 cubic centimeters of the water have passed over and been Nesslerized for free ammonia, remove the burner for a few moments, add 50 cubic centimeters of a solution of potassium hydrate and potassium permanganate, return the burner to its place, and continue the distillation. Collect the distillate in portions of 50 cubic centimeters each, and Nesslerize just as in the determination of free ammonia, continuing the operation as long as a distillate gives a reaction with Nessler reagent. The total amount of ammonia found in this way after the potassium hydrate and permanganate solution is added, is the albuminoid ammonia formed by the decomposition of the nitrogenous organic matter in 500 cubic centimeters of the water, and this amount in milligrams, multiplied by 2, gives the albuminoid ammonia in the water in terms of milligrams per liter or parts per million.

In laboratories where many water analyses are made, the very handy form of apparatus shown in Fig. 2 is largely used for this process. The flask *a* has a capacity of about 2 liters; it is provided with a ground-glass stopper that fits

perfectly, and has a side neck tube that is bent to point straight downwards when the flask is held in the clamp *b* over the burner *c*. The side neck tube is connected with the zigzag tube passing through the vertical condenser *d*, and the Nessler cylinders are held in the rack *e* in such a way that they pass successively under the zigzag tube to receive the

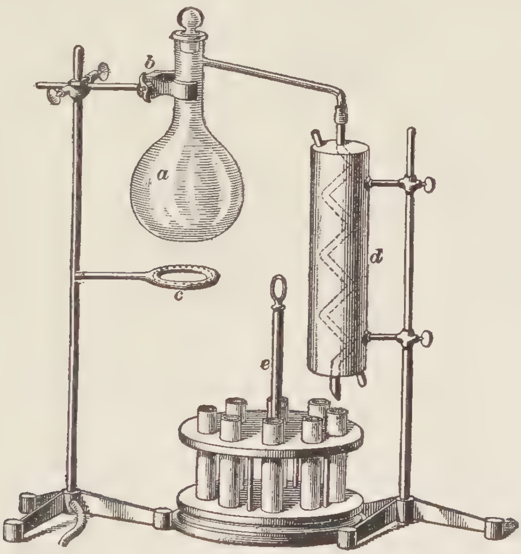

FIG. 2

distillate when the rack is revolved. When using this apparatus, measure the sample into the flask *a*, insert the stopper tightly, light the burner *c*, and proceed with the determination exactly as when a retort is used.

23. Significance of Ammonia.—Nearly all natural waters contain minute quantities of free ammonia, and this in itself is not injurious; but an increase in the amount of this constituent points to unhealthy conditions. It has been suggested that free ammonia is produced in water by the breaking up of albuminous matter before the water is examined, thus indicating that the water is undergoing purification, but that it is not yet sufficiently pure for

domestic use. Water that is contaminated with urine yields a relatively large amount of free ammonia. For this reason, it is sometimes spoken of as *ureal* ammonia, and is regarded as an indication that the water is polluted with sewage. It is the writer's experience, however, that free ammonia sometimes comes from other sources. The amount of free ammonia in water varies with the source. It is usually greater in wells than in streams or ponds. Chemists differ as to the amount that may be present without danger to health. It may be stated, however, that water from a stream or pond containing more than .1 part per million should never be used, and, to be considered as very pure, it should contain considerably less than this.

Although chemists differ somewhat in regard to the significance of free ammonia, they all agree that a relatively large amount of albuminoid ammonia indicates a very dangerous condition, and that a water yielding a very large amount of this constituent should be condemned without qualification. The albuminous matter in water may be either of animal or vegetable origin. The former is regarded as the most dangerous, but the latter, if present in excessive quantity, is almost certain to cause disease. If familiar with the surroundings, the character of the organic matter in a sample of water may be inferred from its source. Another indication is obtained when the water is distilled in the determination of ammonia. The albuminoid ammonia derived from animal matter usually comes over more rapidly and regularly than that from vegetable matter. Much may also be inferred from the results of the other determinations. Water containing vegetable matter alone is frequently almost free from chlorine and free ammonia, while the albuminoid ammonia is relatively high. On the other hand, water polluted with sewage always contains an increased amount of chlorine, and, generally, free ammonia also. Wanklyn, who devised this process, says that the albuminoid ammonia should never exceed .15 part per million, and this limit undoubtedly holds in the case of wells and other waters that may contain sewage contamination.

Chemists are at present inclined to allow a little more in the case of streams and ponds in thickly wooded districts, where the organic impurity consists principally of dead leaves; but, in this case, the water should not contain more than .35 part per million of albuminoid ammonia. In any case, it should be remembered that in order to be regarded as very pure, the water should contain considerably less than these figures given as limits.

SOLUTIONS FOR THE AMMONIA PROCESS

24. Absolute Water.—Ordinary distilled water cannot be used in making the solutions used in the ammonia process, for it contains enough ammonia to render it useless for this purpose, and ammonia-free water, known as absolute water,. must be prepared. The best way to do this, is to make use of the fact that when water is distilled, the free ammonia all passes over with the first third of the distillate, the second third of the distillate is free from ammonia, and the last third contains the remainder of the ammonia. Place a convenient quantity—say 15 liters—of good drinking water in a distilling apparatus and apply heat. Discard the first 5 liters of distillate, then test a little of the distillate with Nessler reagent, and, if it is free from ammonia, collect the next 5 liters, and then stop the distillation. The portion collected will be free from ammonia, and is known as absolute water. The first portion passing over should not be thrown away, as it is sufficiently pure for ordinary use as distilled water. The portion remaining in the distilling apparatus should be thrown out, however, and the apparatus should be rinsed out with fresh water. The absolute water should be kept in glass-stoppered bottles, and it is best to cover the tips with caps to prevent the deposition on them of ammonium compounds from the air of the laboratory. It should be used within a reasonable time after it is prepared, for after standing a long time in the bottles, it will give a cloudy solution when Nessler reagent is added, and is therefore useless for this purpose.

25. Sodium Carbonate.—This solution is made by dissolving 50 grams of pure sodium carbonate in 250 cubic centimeters of absolute water. It should be kept in a bottle with a ground-glass stopper, but care must be taken to keep the stopper from sticking. The object of the solution is to expel any so called free ammonia that is combined with an acid. Its use would not be necessary in many cases, but, for the sake of uniformity, it should be added to every sample. It may be stated here that perfect uniformity of conditions is essential for success in water analysis.

26. Nessler Reagent.—Dissolve 15 grams of mercuric chloride in about 500 cubic centimeters of absolute water. Dissolve 35 grams of potassium iodide in about 200 cubic centimeters of absolute water. Pour the first solution into the second, until a faint, permanent, red precipitate begins to form, adding the mercuric chloride cautiously towards the last. The solution at this point should contain a very slight red precipitate that does not redissolve, even upon vigorous stirring. It now remains to make it strongly alkaline, and to render it sensitive. To do this, add 160 grams of pure solid potassium hydrate, and when it has dissolved and the solution has cooled, dilute it to 1 liter with absolute water, and mix it thoroughly. If potassium hydrate is not at hand, 120 grams of pure sodium hydrate may be substituted for it. The slight reddish precipitate in the solution will be dissolved by the potassium hydrate, and more mercuric chloride must now be added to render the solution sensitive. A cold saturated solution in absolute water is used. Add it cautiously until the last drop added produces a permanent precipitate, and allow this to settle. The clear supernatant liquid should now have a slight yellowish tint, and, if colorless, it is never sensitive. In this case, a little more mercuric chloride must be added, and, after being thoroughly mixed, the solution must be allowed to settle again.

The solution should next be tested to ascertain its condition. For this purpose, measure a quantity of the dilute standard

ammonia solution, containing .01 milligram of ammonia, into a Nessler cylinder; dilute it to 50 cubic centimeters with absolute water, and add 2 cubic centimeters of the solution to be tested. If it is sufficiently sensitive, a yellowish-brown tint will be imparted to the solution in the Nessler cylinder almost immediately. If a distinct color is not developed in the course of half a minute, the solution is not sufficiently sensitive. In this case, add more mercuric chloride, mix thoroughly, allow it to settle, and test again. The stock of Nessler reagent should be kept in a tightly stoppered bottle, and, from time to time, small quantities of it are poured into a small bottle, from which it is drawn as it is used.

27. Standard Solution of Ammonia.—A dilute solution of ammonium chloride is used as a standard in Nesslerizing. It is made up as follows: Dissolve 3.14 grams of pure ammonium chloride in absolute water, dilute to exactly 1 liter with absolute water, and mix the solution thoroughly. This solution is of such strength that 1 cubic centimeter of it contains 1 milligram of ammonia NH_3, and is therefore much too strong for use in Nesslerizing. By means of a burette, measure exactly 10 cubic centimeters of this solution into a liter flask, dilute it to the mark with absolute water, and mix it thoroughly. This solution contains .01 milligram of ammonia in 1 cubic centimeter, and is therefore of a convenient strength to use in Nesslerizing. This solution should be kept in a glass-stoppered bottle, the lip of which is protected from ammonium compounds in the air by means of a cap. In examining extremely bad waters, it is sometimes handy to have a stronger standard solution of ammonia. Such a solution is made by diluting 100 cubic centimeters of the strong solution first made up to 1 liter. This solution will be of such strength that 1 cubic centimeter of it contains .1 milligram of ammonia.

28. Potassium Hydrate and Permanganate.—This solution, which is used to decompose the nitrogenous organic

matter, and set free the albuminoid ammonia, is made as follows: Dissolve 8 grams of pure crystallized potassium permanganate and 200 grams of potassium hydrate in 1 liter of distilled water. Boil the solution until about one-fifth of it has evaporated, and add sufficient absolute water to bring the volume of the solution up to 1 liter when it is cold. Keep the solution in a glass-stoppered bottle, and, when not using it, move the stopper every few days, to keep it from sticking. This solution must always have the reddish-violet color of permanganate. If it becomes green, either in the stock bottle or in the retort when in use, no reliable results can be obtained with it, and a fresh solution must be made up.

29. Practical Suggestions.—If many analyses of water are made, it is best to set apart a portion of the laboratory for this purpose exclusively, and to keep it as free from fumes as possible. The ammonia process cannot be carried out successfully in a laboratory filled with ammonia fumes. It is best to keep the apparatus used in the ammonia process for that purpose alone. At all events, it should not come in contact with organic matter. The apparatus must be thoroughly cleaned before it is used. It is not sufficient to clean it before putting it away, and then to use it without a second washing, for ammonium compounds from the air may be deposited in sufficient quantity to vitiate the results. It is not usually necessary to employ distilled water in washing the apparatus. If washed with a large quantity of good tap water and allowed to drain, it will be perfectly clean; and, under no circumstances, should apparatus used in water analysis be wiped with a cloth.

THE MOIST COMBUSTION PROCESS

30. Before the ammonia process came into general use, chemists tried to estimate the amount of organic matter in water by the amount of oxygen required to oxidize it, using potassium permanganate to supply the oxygen. The methods employed were rather crude, and the results obtained were

unsatisfactory, as, in many cases, only a small fraction of the organic matter was oxidized. At present, the so called moist combustion process is largely used, and it is believed that by this method the organic matter in a water is oxidized, and the amount of oxygen used may be accurately measured. It has been objected to this process that when two samples are treated, one of which contains vegetable matter, and the other an equal amount of animal matter, the water containing the vegetable matter will consume the larger quantity of oxygen, while that containing the animal matter is undoubtedly the more dangerous.

While the results obtained by this method are probably not so important as those obtained by the ammonia process, they are of value inasmuch as they give a further idea of the amount of organic matter in a sample, and also of its character. It has been stated that the weight of organic matter in a liter of water is approximately equal to the weight of oxygen consumed when a liter of the water is subjected to the moist combustion process. While this statement is correct when the organic matter is starch and some other compounds, it will not hold good in all cases, and, consequently, the results should be stated in milligrams of oxygen consumed, without attempting to state the weight of organic matter present.

The amount of oxygen that may be consumed by the carbonaceous matter in a liter of water without rejecting it for domestic use, is not so clearly defined as in the case of ammonia. In fact, the results obtained by this process are more largely used to throw light on the results of the ammonia process than to establish the quality of the water, when considered by themselves. It may be stated, however, that to be considered of first-class quality, a liter of the water should not consume much more than 1 milligram of oxygen. Many drinking waters that are considered wholesome consume from 1 to 3 parts of oxygen per million, but anything above this should be regarded with suspicion, and a water, 1 liter of which consumes more than 5 milligrams of oxygen, should usually be rejected. The details of the process are as follows:

31. Determination of Oxygen Consumed.—Mix in a flask 200 cubic centimeters of the water to be examined with 10 cubic centimeters of the dilute sulphuric acid. Heat rapidly until the water is just about to boil, and run in from a burette the standard potassium-permanganate solution until the water has a decided red color. Boil 10 minutes, watching carefully and adding more permanganate as the color fades. Do not allow the color to fade nearly out before adding more permanganate; but add the permanganate so as to keep the color constant. Remove the lamp, and add from another burette sufficient standard oxalic-acid solution to destroy the color; 10 cubic centimeters is generally the right amount. Then add the permanganate until a faint pink color again appears. From the total amount of permanganate used deduct that corresponding to the oxalic acid used, and from the remainder calculate the number of milligrams of oxygen consumed by the 200 cubic centimeters of water. This multiplied by 5 will give the number of milligrams consumed per liter.

32. In case the water contains nitrites, ferrous salts, or hydrogen sulphide, corrections for these substances, which also reduce permanganate, must be made.

SOLUTIONS REQUIRED

33. Standard Potassium Permanganate.—Dissolve .395 potassium permanganate in distilled water, and dilute to 1 liter. Each cubic centimeter of this solution contains .0001 gram available oxygen. The available oxygen in the presence of sulphuric acid and easily oxidized substances may be represented by the equation:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

34. Standard Oxalic Acid.—Dissolve .7875 gram pure oxalic acid $C_2H_2O_4 \cdot 2H_2O$ in distilled water and dilute to

1 liter. This solution if titrated with the permanganate solution while hot and acid with sulphuric acid should correspond with it cubic centimeter for cubic centimeter. The solution, however, does not keep well, and in practice it is necessary to standardize the solution by adding 10 cubic centimeters of the oxalic acid to 200 cubic centimeters of distilled water and 10 cubic centimeters of the dilute sulphuric acid. This is heated to boiling and titrated by the standard permanganate solution. From the number of cubic centimeters of permanganate used the value of the oxalic acid is calculated. This standardizing should always be done the same day a determination is made.

35. Dilute Sulphuric Acid.—Mix 1 volume of pure concentrate sulphuric acid with 3 volumes of distilled water and drop in sufficient permanganate solution to give a very faint pink color. Heat to 60° C., and keep at that temperature 2 hours. If the color disappears, add more permanganate until it leaves the solution a very faint pink after heating 2 hours to 60° C.

NITROGEN AS NITRITE

36. It is generally admitted that nitrites found in pond or river water ordinarily come from the putrefaction of nitrogenous organic matter—usually of animal matter. In deep wells, the conditions are somewhat different. These waters may contain nitrites that have been formed by the deoxidation of nitrates in percolating through strata containing mineral reducing agents.

37. Professor Mallet considers this determination of great importance, and the writer's experience agrees perfectly with this view. At all events, the result of this determination should be kept in mind in deciding the quality of a water, and, when nitrites are present, the results of the other determinations should be interpreted with greater strictness than when they are absent. Professor Mallet examined eighteen samples

of water from different sources, all of which were believed to be wholesome, and found that the average of the eighteen samples was .0135 part of nitrogen as nitrite in a million parts of water. He also examined nineteen samples of waters that were thought to have caused disease, and found the average to be .0403 part of nitrogen as nitrite per million. It has been the experience of other authorities that the nitrogen as nitrite found in good wholesome water is usually much less than the figures given above.

38. Determination of Nitrogen as Nitrites.—Place a measured quantity, 50 or 100 cubic centimeters, in a Nessler cylinder, add 1 drop of concentrate hydrochloric acid, 1 cubic centimeter of sulphanilic-acid solution, and 1 cubic centimeter of naphthylamine hydrochloride. Mix thoroughly by stirring with a glass rod, cover with a watch glass, and set aside for 30 minutes. Prepare at the same time standard solutions containing known amounts of standard sodium nitrite diluted to 50 or 100 cubic centimeters with absolute water, and the same amount of reagents as above. At the end of 30 minutes compare the depth of the pink color formed in the water to be tested with the various standard solutions in the same way as in the ammonia determination.

SOLUTION FOR NITROGEN AS NITRITES

39. Sulphanilic Acid.—Dissolve 1 gram of sulphanilic acid in 100 cubic centimeters of hot water, cool, and preserve in a stoppered bottle.

40. Naphthylamine Hydrochloride.—Boil .5 gram of naphthylamine hydrochloride with 100 cubic centimeters of water for 10 minutes, adding water to make good any evaporation. When cool, transfer to a stoppered bottle and preserve in a dark place.

41. Standard Nitrite Solution.—The sodium or potassium nitrite sold by chemical dealers is not pure enough to

be used for this purpose, and, consequently, silver nitrite is employed in its preparation. This salt may be obtained from dealers, but, in order to be sure of its purity, it is best to prepare it. This is done as follows: Make up strong solutions of silver nitrate and sodium or potassium nitrite, using a very little more of the nitrite than the calculation would indicate as necessary. Heat both solutions just to the boiling point, mix them, and filter at once. The silver nitrite formed dissolves quite readily in boiling water, but crystallizes from the filtrate as it cools. When quite cold, pour off the mother liquor, wash the crystals once by decantation with a little cold water, dissolve them in a little boiling water, filter and recrystallize. Wash these crystals once by decantation with a little cold water, drain this off and dry them, at first over a water bath, and, finally, in a desiccator. When dry, the crystals will consist of pure silver nitrite, 11 grams of which contain 1 gram of nitrogen. The salt must not be exposed to a strong light, either during or after preparation. Continued boiling must also be avoided, as this tends to slowly decompose the silver nitrite with the formation of nitrate.

Weigh out .275 gram of the pure silver nitrite, dissolve it in a little hot water, and add a slight excess of sodium-chloride solution. This will precipitate the silver as chloride, and form a corresponding amount of sodium nitrite. Filter off the silver chloride, wash the precipitate with absolute water until the filtrate and washings amount to exactly 250 cubic centimeters, and mix this solution thoroughly. Measure out exactly 10 cubic centimeters of this solution, dilute it to 1 liter, mix it thoroughly, and keep it in a tightly stoppered bottle. The liter of solution contains 1 milligram of nitrogen in the form of nitrite, and, consequently, each cubic centimeter contains .001 milligram of nitrogen.

42. In comparing colors, if 100 cubic centimeters of water are taken, and its color is found to match that of the solution in the cylinder containing 3 cubic centimeters of the standard nitrite solution, it shows that 100 cubic centimeters

of the water contain .003 milligram of nitrogen, and that 1 liter contains .03 milligram of nitrogen as nitrite. Or, as it is more frequently stated, the water contains .03 part per million of nitrogen as nitrite.

NITROGEN AS NITRATE

43. The nitrates in water are generally believed to come principally from the oxidation of nitrogenous organic matter, and it has been asserted that when the nitrogen reaches this state of oxidation, all danger is past, and the nitrates can only be considered as an evidence of past pollution. Experience does not support this statement, for water containing 5 parts per million of nitrogen as nitrate, though the albuminoid ammonia was low, has been known to cause disease. The amount of nitrogen in the form of nitrate ordinarily present in a water depends on its source. In ponds and streams, the quantity is generally rather less than .2 part per million, while in wells, it sometimes reaches ten times this figure. It is probably safe to say that a well water containing over 3 parts per million should be regarded with suspicion. There are a number of methods for the determination of nitrogen existing as nitrate in water. The one given in this Section is largely used and is very satisfactory.

44. The Picric-Acid Test.—The picric-acid, or the phenol-sulphonic, test depends on the fact that when phenol and sulphuric acid are added to a sample of water, the nitric acid in the water converts a corresponding amount of the phenol into picric acid, and, when an excess of ammonia is added to this, a yellow color is produced, the depth of which depends on the amount of picrate present. By comparing this color with that produced when a solution containing a known quantity of nitrate is similarly treated, the amount of nitrogen existing as nitrate in the water is obtained. The details of the process are as follows: Dissolve .7214 gram of pure potassium nitrate in absolute water, and dilute the solution to exactly 1 liter for a stock standard solution. This

solution is then of such a strength that 1 liter contains 100 milligrams of nitrogen, and, consequently, 1 cubic centimeter contains .1 milligram of nitrogen. When ready to make the determination, measure exactly 10 cubic centimeters of the stock solution into a 100-cubic-centimeter flask, dilute it exactly to the mark, and mix it thoroughly. A solution is thus obtained, 1 cubic centimeter of which contains .01 milligram of nitrogen. Measure 10 cubic centimeters of this diluted solution into a small porcelain dish, and into a similar dish measure 10 cubic centimeters of the water to be tested;* place them side by side on water baths, and evaporate to apparent dryness. As soon as the residues appear to be dry, or even while they appear slightly moist, remove the dishes from the water baths. Heating after the residue is dry is almost sure to cause inaccuracies, for nitric acid is slowly expelled by the heat, and some nitrate may be absorbed by the residue from the products of combustion if a gas flame is used in heating the water.

While the sample and standard are evaporating to dryness, mix 6 drops of concentrate phenol and 30 drops of concentrate sulphuric acid. Several methods of making up a stock solution of this reagent have been proposed, but it is found that much more satisfactory results are obtained by making up a small quantity of it just before it is used. Add about 10 drops of this solution to each dish, taking care to add the some quantity to each. Then, by means of glass rods, spread this solution around so that it moistens every particle of the residue. Add 1 cubic centimeter of concentrate sulphuric acid to each dish, and warm them for 2 or 3 minutes on the water bath. Then remove them, allow them to cool, add 10 cubic centimeters of water to each, stir them up, add 5 cubic centimeters of concentrate ammonia to each, and stir them again, whereupon the color will develop. Rinse the solution from the sample into a Nessler cylinder, dilute it to 50 cubic centimeters, and treat the standard as the colors produced indicate as best.

* Add to each 1 drop of the sodium-carbonate solution used in the ammonia determination.

In many cases it will be sufficient to wash it into a Nessler cylinder, dilute to 100 cubic centimeters, mix well, remove small measured portions to other cylinders, dilute them to 50 cubic centimeters each, and compare the colors with that of the sample. As 10 cubic centimeters of the dilute standard are taken, the 100 cubic centimeters in the Nessler cylinder contains .1 milligram of nitrogen, and 1 cubic centimeter contains .001 milligram. If 9 cubic centimeters of this are required to make a solution that, when diluted to 50 cubic centimeters, matches the color of the standard, it shows that 10 cubic centimeters of the water under examination contain .009 milligram of nitrogen existing in the form of nitrate, and, therefore, 1 liter of the water contains .9 milligram, or the water contains .9 part per million of nitrogen as nitrate. In examining very pure samples of water, it is sometimes necessary to evaporate a larger quantity, in order to get a color that is strong enough for accurate comparison. As much as 50 cubic centimeters is sometimes required.

It has been asserted that this method does not yield accurate results with samples containing much chlorine, and this appears to be true if the reagent is made up in considerable quantity and allowed to stand some time before it is used, and may be true in extreme cases even when a fresh solution is used. We have obtained very accurate results by using a freshly prepared solution even in the presence of a large amount of chlorine, and it is stated by some chemists that when the fresh reagent is employed, chlorine has no effect on the results, even though an excessive amount of it may be present. The nitrogen existing as nitrite does not interfere with this determination, as nitrous acid forms nitrosophenol, which is colorless in dilute solution.

POISONOUS METALS

45. Probably the poisonous metals most frequently occurring in water are copper, lead, and zinc. They are sometimes found in the natural water in the regions where these metals are mined, and some waters have the power of acting

on lead or copper pipes or fixtures, dissolving these metals; or on galvanized iron pipes or vessels, dissolving zinc. Arsenic and chromium, both of which are poisonous, sometimes occur in water, and iron occurs in small quantities in many waters. This latter element, though not generally considered very poisonous, is, nevertheless, very objectionable when present in considerable quantity. When any of these metals are present, they should not be overlooked. For lead, copper, and iron, very simple colorimetric methods may be used.

46. Lead and Copper.—The method generally employed in determining these metals is due to Miller. It consists in comparing the depth of the colors produced by adding ammonium sulphide to the sample and to a standard solution. The details of the process are as follows: Make up a standard solution of lead nitrate by dissolving 1.599 grams of the pure salt in water and diluting to exactly 1 liter. Each cubic centimeter of this solution will contain 1 milligram of metallic lead. Now measure 100 cubic centimeters of the water to be tested into a Nessler cylinder, add 5 drops of concentrate hydrochloric acid, then 1 cubic centimeter of colorless ammonium sulphide, and stir the solution. Into a similar cylinder, measure a small quantity of the standard lead solution, dilute to 100 cubic centimeters, add 5 drops of concentrate hydrochloric acid, 1 cubic centimeter of colorless ammonium sulphide, stir well, and compare the color produced with that of the sample. Prepare other standards in the same way until one is obtained, the color of which exactly matches the sample. The minute quantity of copper or lead usually contained in water contaminated with these metals, will give the sample a brownish color, due to the formation of the dark sulphide. If the water is rendered alkaline by the addition of the ammonium sulphide, the color may be due to iron; hence, after the color has been obtained, the sample and standard should be rendered distinctly acid with dilute hydrochloric acid, adding the same amount of acid to each. A diminution or disappearance of color in the

sample, when thus treated, indicates that the color is due, either partially or wholly, to iron, the sulphide of which is dissolved by dilute hydrochloric acid.

This method, of course, will not distinguish between copper and lead, but, as both metals are poisonous, this is not usually necessary, and the approximate quantity of the two metals may be estimated as above if both are present. If it is required to know which metal is present, a large quantity of the water must be evaporated to a small bulk, and a qualitative analysis made. If copper alone is found to be present, a standard solution of copper sulphate, containing 1 milligram of metallic copper in a cubic centimeter, is made up, and a colorimetric determination made, just as when the lead solution is used. A standard copper solution for this purpose is made by dissolving 3.927 grams of pure crystallized copper sulphate in distilled water, and making the solution up to 1 liter.

It is sometimes desirable to know the action of a certain water on lead pipe. To learn this, place a piece of bright lead in one vessel, and a piece of dull lead in another; cover them with the water, allow them to stand 24 hours, and then examine each sample for lead as directed above.

47. Iron.—Wanklyn states that good drinking water should not contain more than 3 parts of iron per million. This limit may be rather severe, but it is undoubtedly true that a good drinking water should not contain a large amount of iron. Water to be used in washing white goods, or in dyeing, should also contain but little of this element. To determine iron, acidify a suitable volume (200 to 500 cubic centimeters, according to indications) of the water with aqua regia, evaporate this solution to 100 cubic centimeters, pour it into a Nessler cylinder, and add 2 cubic centimeters of ammonium-sulphocyanide solution. Compare the color thus produced with the colors of standards made by adding measured quantities of standard iron solution to Nessler cylinders, diluting to 100 cubic centimeters with distilled water, and adding 2 cubic centimeters of ammonium sulphocyanide.

To make the standard solution of iron, weigh .1 gram of pure iron into a small beaker, and dissolve it in a little hydrochloric acid; add a few drops of nitric acid, and heat to boiling. Wash this solution into a liter flask, and dilute it to the mark with distilled water that is known to be free from iron. Each cubic centimeter of this solution contains .1 milligram of iron.

48. Zinc and Chromium.—These metals are best determined by evaporating a large quantity of the water to a small bulk, and applying the usual gravimetric methods. The quantitative estimation should be preceded by a qualitative examination of a concentrated sample, and the exact method of procedure made to depend on what is thus learned. In any case, acidulate a large quantity of the water with hydrochloric acid, evaporate to dryness, and heat in an air bath at 120° to 130° until the odor of hydrochloric acid is no longer perceptible. Moisten the residue thoroughly with concentrate hydrochloric acid, and add an appropriate quantity of water, the amount depending on the size of the residue. Heat this solution to boiling, filter off the silica, and wash it thoroughly with hot water. If first or second group metals are present, they must be precipitated by hydrogen sulphide, and the filtrate must be boiled to expel the last trace of this reagent. If the qualitative test has indicated that only chromium and zinc are now present, heat the water to boiling, and slowly add a slight excess of dilute ammonia while stirring continuously. Filter off the precipitated chromium hydrate, and proceed with the determination of chromium as directed in *Quantitative Analysis*, Part 1.

Concentrate the filtrate from the chromium hydrate to a convenient volume, render it distinctly alkaline with sodium carbonate, and then add sufficient acetic acid to render it slightly but distinctly acid, and dissolve any precipitate formed by the carbonate. Heat the solution to incipient boiling, and precipitate the zinc as sulphide by leading a rather rapid current of hydrogen sulphide through the

solution. The zinc may be weighed as sulphide, or the precipitate may be dissolved, and the zinc determined in the solution by one of the methods given in the foregoing Sections.

49. Arsenic.—Arsenic occurs in some waters, and, when present, it should not be overlooked. A qualitative determination is all that is ordinarily required, and for this purpose the Marsh test is generally employed. The details of this process are given in *Qualitative Analysis*, Part 4. When pure zinc is employed in making this determination, the action is very slow at first, and the process becomes quite tedious. Zinc, alloyed with platinum for this purpose, is now on the market, and it appears to be a decided improvement.

If a quantitative determination is required, a large quantity of the water should be evaporated to the proper volume, and the arsenic determined in this by one of the methods previously given.

HARDNESS

50. The determination of hardness has more to do with the scale-forming constituents of a water than with those that have an influence on its character as a drinking water, and, consequently, is probably of greater value in the examination of water for a boiler supply than in the analysis of potable waters. But if the water is for domestic use, a knowledge of how it will act in cooking utensils is of value, and this determination is of considerable importance in examining a water that is to be used for laundry purposes. It is a well known fact that when soap is added to a water containing salts of calcium or magnesium, a considerable portion of the soap is used up in precipitating these metals before any of it is available for detergent purposes. Waters containing these salts are spoken of as hard waters. They are not adapted for laundry use on account of the increased amount of soap required, and the precipitate formed in the water is

undesirable. As we have seen, hardness is divided into permanent and temporary hardness. Temporary hardness is due to salts that are precipitated by boiling the water, and permanent hardness is due to those that remain in solution after the water is boiled. As a rule, the total hardness is all that is required.

Dr. Clark devised a method for the estimation of the hardness of a water by means of a standard soap solution. The soap solution is added to the water until a permanent lather forms, and the hardness is thus learned. This method is in some respects unscientific, but it is nevertheless valuable in many instances. The results were formerly stated in degrees of hardness, and this would be the best method of reporting results if so much confusion had not entered through the use of different quantities of sample; but as degrees based on different quantities are used, such a report is without meaning unless accompanied by an explanation. To avoid confusion, we prefer to state results in parts per million of calcium carbonate or its equivalent.

51. Standardizing the Soap Solution.—Scrape 10 grams of shavings from a new cake of pure Castile soap, dissolve them in 1 liter of dilute alcohol (2 parts of absolute alcohol to 1 part of water), filter off insoluble matter, if any is present, and keep the solution in a glass-stoppered bottle. To ascertain the strength of this solution, weigh out exactly 1 gram of pure calcium carbonate, and dissolve it in the least necessary quantity of dilute hydrochloric acid. Cautiously add dilute ammonia in sufficient quantity to just neutralize the excess of acid, and dilute the solution to 1 liter. Each cubic centimeter of this solution will contain a quantity of calcium salt equivalent to 1 milligram of calcium carbonate.

Measure 10 cubic centimeters of this standard calcium solution into a glass-stoppered bottle having a capacity of about 250 cubic centimeters, and add 90 cubic centimeters of distilled water. Then add soap solution, .5 cubic centimeter at a time, and shake after each addition, until a lather

is formed that persists for 5 minutes. Note the quantity of soap solution used, and then repeat the experiment, adding .5 cubic centimeter of solution at a time at first, but only .1 or .2 at a time towards the end of the reaction. The exact amount required is thus learned. Now cleanse the bottle, introduce 100 cubic centimeters of pure distilled water, and titrate this with the soap solution in the same way, to learn the amount of soap solution used up by 100 cubic centimeters of pure water. Subtract this amount from the amount used in titrating the standard, to learn the amount used in precipitating the calcium. From this, calculate the value of 1 cubic centimeter of the soap solution in terms of calcium carbonate, and record the factor thus found on the bottle, together with the date of standardization.

An example may render this more clear. Let us suppose that 10 cubic centimeters of the soap solution are used up by the standard, consisting of 10 cubic centimeters of calcium solution and 90 cubic centimeters of distilled water, and that .8 cubic centimeter is used up by 100 cubic centimeters of distilled water. Then, 9.2 cubic centimeters of the soap solution are required for 10 milligrams of calcium carbonate, and the value of 1 cubic centimeter of soap solution in milligrams of calcium carbonate is 1.087. The soap solution should be restandardized at frequent intervals, for it is not permanent, and deteriorates quite rapidly, especially in cold weather.

52. Determination of Hardness.—Measure 100 cubic centimeters of the water into a glass-stoppered bottle of about 250 cubic centimeters capacity, and add soap solution, .5 cubic centimeter at a time, shaking after each addition, until a lather that persists for 5 minutes is formed. When a permanent lather appears to be formed, place the bottle on its side, and allow it to remain in this position for 5 minutes, or until the lather disappears. If the lather disappears in less than 5 minutes, add a little more soap, shake, and again place the bottle on its side. When the lather persists for

5 minutes, the reaction is complete. Now, from the amount of soap solution used, deduct the amount required to produce a permanent lather with 100 cubic centimeters of distilled water, multiply this quantity by the value of 1 cubic centimeter of the soap solution, and multiply the result thus obtained by 10. The total hardness of the water, expressed in parts of calcium carbonate or its equivalent per million, is thus obtained.

In order to obtain the most concordant results, the soap solution should be standardized, and all determinations made at the same temperature, preferably at 15°. It should be remembered that the method is not strictly accurate at best, and, to obtain concordant results, the same method of procedure should be adopted in every case. This is important in adding the soap solution. Not more than .5 cubic centimeter of this should be added at a time, even though the approximate amount required is known. If a water is so hard that 100 cubic centimeters of it require more than 20 cubic centimeters of the soap solution, a second determination should be made, using 50 cubic centimeters of the sample and 50 cubic centimeters of distilled water. Better results are obtained in this way, for the large precipitate formed in the undiluted sample appears to interfere with proper lathering.

It is usually sufficient to determine the total hardness, but, in some cases, the temporary and the permanent hardness are required. When this is the case, determine the total hardness; then boil 100 cubic centimeters of the water, filter off any precipitate formed, add distilled water to make up for the portion evaporated, and determine the permanent hardness in this sample. The difference between the total hardness and the permament hardness is the temporary hardness.

INTERPRETATION OF RESULTS

53. In no branch of chemical work is the exercise of judgment more necessary than in forming an opinion as to the quality of potable water from the results obtained by

analysis. The chemist should make himself as familiar as possible with the history of the water, and then should consider all the results together in the light of all that is known of the water, and in regard to their bearing on each other. In the case of very good or very bad waters, it is a comparatively easy matter to decide as to their quality; but, with many samples lying between these two extremes, the most careful study is required. The following figures, taken from the standards of purity of drinking water specified by the Michigan State Laboratory of Hygiene, may be of value to the student:

1. The total solids should not exceed 500 parts per million.

2. The chlorine should not exceed 12.1 parts per million.

3. The free ammonia should not exceed .05 part per million.

4. The albuminoid ammonia should not exceed .15 part per million.

5. The oxygen consumed by organic matter should not exceed 2.2 parts per million.

6. The nitrogen as nitrate should not exceed .9 part per million.

7. The best water contains no nitrous acid, and any water that contains nitrites in quantity sufficient to be estimated should not be regarded as a safe drinking water.

These dogmatic statements should not be accepted as final, and indeed no fixed limits can be prescribed, but, as we have pointed out, the results must be considered in their relation to one another, and in the light of what is known of the water. For example, a water contaminated by sewage, and found to contain 12.1 parts per million of chlorine, and .15 part per million of albuminoid ammonia, should be condemned absolutely; while the water of a pond or stream in a heavily wooded district containing salt deposits, might contain these quantities of the constituents mentioned, and still be fairly wholesome.

EXAMINATION OF ICE

54. Chemists are frequently called on to examine samples of ice. In such cases, the ice is allowed to melt, and the water thus obtained is examined in the usual manner. It should not be allowed to melt exposed to the air, however, but should be enclosed in a jar with a tight-fitting glass stopper. A 2-gallon jar with a wide mouth serves well for the purpose. Wash the jar well with distilled water, and introduce the ice in as large pieces as possible, taking care not to touch the ice with the hands more than is necessary. Small fire-tongs, thoroughly cleaned, serve well in handling the ice. Insert the stopper, and allow about one-fifth of the ice to melt at the temperature of the room. Pour off the water, thus thoroughly washing the remaining ice, insert the stopper again, and allow the rest of the ice to melt. Using the water thus obtained as a sample, make the ordinary determinations in the usual manner.

Free ammonia may be present in ice* in about the same quantity as in the water from which it is obtained, but, for the other constituents, the limits of purity are lower.

WATER FOR BOILER SUPPLY

55. Little is cared about the sanitary quality of a water to be used as a boiler supply, but the mineral or scale-forming constituents of the water are important in this case. The principal scale-forming constituents are the carbonates of calcium and magnesium, and calcium sulphate; but, in order to learn the quantities of these constituents present, it is necessary to determine other constituents not generally considered as scale-forming. Sometimes the determination of two or three constituents is all that is required, but such an examination would prove of little service in many cases. A method that will give the most complete idea of the water

* Artificial ice made by the ammonia process frequently contains large amounts of free ammonia due to leaks in the apparatus; such ice may still be perfectly wholesome.

obtainable by the ordinary methods of analysis, is as follows: First determine the total solids as previously directed, as this will serve as a guide in later work, and then proceed with the analysis of the mineral residue. While carrying on this analysis, determine the chlorine and the hardness as previously directed.

56. Determination of Silica.—Measure out an appropriate quantity of the water (from 1 to 10 liters, depending on the amount of solids found), acidify it with hydrochloric acid, and evaporate to dryness in a platinum dish. The evaporation may be carried on over a Bunsen burner, adding successive portions of the water until the sample is all in the dish, and reduced to rather small bulk, but should be completed over a water bath. When dry, remove the dish from the water bath to an air bath, and heat it at 120° to 130° until the odor of hydrochloric acid is no longer perceptible. Moisten the residue thoroughly with concentrate hydrochloric acid, add from 25 to 50 cubic centimeters of water, and boil to dissolve the soluble salts. Filter, wash thoroughly with hot water, ignite in a platinum crucible, and weigh.

If the residue is very small, it is almost certain to be composed entirely of silica, and an examination is scarcely necessary; but if it is of any considerable size, it may contain calcium sulphate, and should be treated as follows: Fuse the residue with sodium carbonate, dissolve the fusion in water and hydrochloric acid, evaporate to dryness, and heat at 120° to 130° to render the silica insoluble. Moisten the residue with hydrochloric acid, add 25 to 50 cubic centimeters of water, and boil to dissolve soluble salts. Filter off the insoluble residue, wash thoroughly with hot water, ignite, and weigh as silica SiO_2.

Heat the filtrate from the silica to boiling, add ammonia to render it alkaline, and then ammonium oxalate to precipitate the calcium; allow it to stand for at least 3 hours, filter, wash, ignite, and weigh as calcium oxide. Calculate this to calcium sulphate, for this portion of the calcium, at least, occurs as sulphate in the water.

57. Determination of Iron Oxide and Alumina. Heat the filtrate from the first insoluble residue to boiling, and cautiously add a very slight excess of ammonia. If a copious light-colored precipitate separates, it may contain calcium. In this case, add a little more ammonia, and then dissolve the precipitate in a slight excess of hydrochloric acid. Enough ammonium chloride will thus be formed in the solution to prevent the precipitation of calcium. Now render the solution faintly alkaline with ammonia, continue the boiling for a few moments, allow the precipitate to settle, and filter off the hydrates of iron and aluminum. Wash the precipitate with hot water, ignite in a platinum crucible, and weigh as the oxides of iron and aluminum $Fe_2O_3 + Al_2O_3$. It is unnecessary to separate the oxides in this case, and they should be reported as they are weighed.

58. Determination of Calcium.—At this point, the filtrate will usually be rather large, and should be evaporated to a suitable volume. Then, to the gently boiling liquid, add a few cubic centimeters of ammonia and a moderate excess of ammonium oxalate, continue to boil for a few minutes, and allow the precipitate to settle. Filter, wash thoroughly with hot water containing a few drops of ammonia, ignite intensely over the blast lamp, and weigh as calcium oxide.

59. Determination of Magnesium.—Evaporate the filtrate from the calcium oxalate to a rather small bulk, add a moderate excess of sodium-ammonium phosphate solution while stirring vigorously, add about one-fourth the volume of the liquid of strong ammonia, and cool the solution by standing it in ice water. If a precipitate begins to form at once, when the microcosmic salt or the ammonia is added, the reagent should be introduced, a drop at a time, and the solution stirred after the addition of each drop. Allow the solution to stand 6 hours in a cool place for the precipitate to settle. Filter, wash with one-third-strength ammonia, ignite intensely, and weigh as magnesium pyrophosphate $Mg_2P_2O_7$. Calculate the magnesium to oxide MgO.

60. Determination of Sulphuric Acid.—Acidulate from 1 to 5 liters of the water with hydrochloric acid, evaporate to a small bulk over a burner, and then to dryness on a water bath. Moisten the residue with hydrochloric acid, dissolve it in water, filter off any silica that remains, and wash it thoroughly with hot water. The filtrate should amount to about 100 cubic centimeters. Heat it to boiling, add a moderate excess of barium chloride, and continue the boiling for a few moments. Allow the precipitate to settle, filter, wash with hot water, ignite moderately, and weigh as barium sulphate. From this, calculate the amount of sulphur trioxide in a liter. If a filter paper is used in filtering, the precipitate should be dried and removed from the paper before ignition, to avoid reduction of the precipitate by the burning paper, and a good quality of paper must be used to avoid danger of the precipitate running through. A Gooch crucible is preferred for this purpose by many chemists.

61. Determination of Alkalies.—Acidulate from 1 to 5 liters of the water with a few drops of hydrochloric acid, and evaporate to about 75 cubic centimeters; then add a saturated solution of barium hydrate as long as it produces a precipitate. Heat to boiling, filter, and wash the precipitate until a test of the washings, acidified with nitric acid, fails to give a reaction for hydrochloric acid on the addition of silver nitrate. Evaporate the filtrate to about 75 cubic centimeters, remove from the burner, add a few drops of ammonia, then a strong solution of pure ammonium carbonate as long as a precipitate forms, and allow the solution to stand for some time, stirring occasionally until the precipitate becomes granular. Filter and wash the precipitate with water containing a very little ammonium carbonate and a few drops of ammonia. After adding a few drops of hydrochloric acid, evaporate the filtrate and washings to dryness in a platinum dish over a water bath, place the dish in an air bath heated to about 100°, and gradually increase the temperature to 130° or 140°. Then cautiously heat the

dish to dull redness over a burner to expel ammonium salts, but take care not to heat it sufficiently to volatilize potassium chloride. Dissolve the residue in about 10 cubic centimeters of water, by the aid of very gentle heat, add a few drops of barium hydrate, then a few drops of ammonia, and a slight excess of ammonium carbonate, and allow the solution to stand a short time, stirring occasionally. Filter and wash the precipitate with water containing a very little ammonium carbonate and a drop or two of ammonia. After adding a few drops of hydrochloric acid, evaporate the filtrate to dryness in a weighed platinum dish over a water bath; place the dish in an air bath heated to about 100°, and increase the temperature to about 140°; then heat it very cautiously over a burner to expel all ammonium salts, cool in a desiccator, and weigh as soon as cool. The residue in the dish now consists of the chlorides of sodium and potassium.

Dissolve the residue of mixed chlorides in the least necessary quantity of water, add a solution of platinum chloride that is as nearly neutral as possible, in excess of the quantity required to unite with all the potassium and sodium present, and evaporate to a pasty consistency on a water bath in which the water is maintained at just about the boiling point, but is not allowed to boil vigorously. Allow the mass to cool, add 35 cubic centimeters of 80-per-cent. alcohol and let it stand in a moderately warm place for an hour, stirring from time to time. If the precipitate is rather large, filter on a paper that has been dried at 120° or in a Gooch crucible, wash thoroughly, but not excessively, with 80-per-cent. alcohol, dry at 120°, and weigh as potassium-platinum chloride K_2PtCl_6. If the precipitate is very small, it is best, after filtering and washing, to dissolve it with a little water; allow the solution to run into a weighed platinum dish, evaporate to dryness on a water bath, heat at 125° in an air bath, cool, and weigh as K_2PtCl_6. Calculate the potassium to chloride, subtract this from the weight of mixed chlorides previously obtained, to get the weight of sodium chloride, and calculate the potassium and sodium to oxides K_2O and Na_2O.

62. Grouping the Constituents.—The most rational method of reporting the results of a mineral analysis of a water would be to report just what is found, without attempting to show how the constituents were combined in the water. This method, however, would only show what scale-forming constituents are present to a person acquainted with chemical combination; and to make the analysis as useful as possible, an attempt is usually made to report the compounds as they exist in the water. Careful experiments have shown that if the constituents are grouped according to the following rule, the report will show what compounds exist in waters ordinarily used as potable water or for boiler supp.y.

Combine the chlorine with the sodium, and if there is more than is required to saturate this, combine it next with potassium; if there is chlorine still left, combine it next with magnesium, and, finally, with calcium. Combine the sulphuric acid with potassium first, if there is any left, and the sodium is not saturated with chlorine; combine the remaining sulphuric acid with the remaining sodium, then with calcium, and, finally, with magnesium. Any of these metals now remaining uncombined are calculated to carbonates. This method of grouping the constituents very nearly represents the facts so far as they can be ascertained for most waters used in boilers and for domestic purposes. There are exceptions to this rule, however, notably in the case of artesian wells, and, especially, mineral waters.

DETERMINATION OF METALS IN ORES

COPPER

63. For the determination of **copper** in ores the methods already given may be used; but as a rapid method of determining copper alone is frequently wanted, a different method of procedure is followed. Three methods are in general use for this determination.

1. *The Electrolytic Method.*—Weigh out an amount of the finely ground ore that will contain from .2 to .4 gram copper, transfer to a casserole, moisten with water, add 25 cubic centimeters of strong nitric acid and 1 cubic centimeter of strong sulphuric acid, cover with a watch glass, and heat until dense choking fumes of SO_3 come off. Cool, moisten with 7 cubic centimeters of dilute (1:1) nitric acid, add 4 drops of strong sulphuric acid and 40 cubic centimeters of water, heat until soluble salts are all in solution. Filter off the insoluble matter and precipitate the copper from the filtrate by electrolysis, as previously described. This method is very extensively used where large numbers of determinations are required. It has the advantage that one man can attend to a large number of analyses; the electrolysis can run at night. On the other hand, it has the disadvantage of requiring expensive apparatus; a single determination cannot be completed as rapidly as by other methods; and care must be exercised to prevent other metals being deposited with the copper.

2. *The Cyanide Method.*—Treat from .5 to 1 gram of finely powdered ore in a flask of about 250 cubic centimeters capacity with 10 cubic centimeters of strong nitric acid, boil down to about 2 cubic centimeters, add 10 cubic centimeters of strong hydrochloric acid, and boil for 3 minutes. Then add 10 cubic centimeters of strong sulphuric acid and boil

until all the hydrochloric and nitric acids are driven off and dense white fumes of SO_3 come off. Allow to cool, and add 10 cubic centimeters of water and about 7 grams of commercial sheet zinc; shake to break up any cake of sulphates. Allow to stand until all the copper is precipitated; 5 minutes is generally long enough. Then add 40 cubic centimeters of water and 20 cubic centimeters of strong sulphuric acid to dissolve the excess of zinc. This is usually complete in 5 minutes. When the zinc has all dissolved, fill the flask with water (tap water may be used) and allow the copper to settle to the bottom; carefully pour off the water, leaving the copper in the flask; fill the flask again with water, allow to settle, and decant the clear liquid. Repeat this washing twice. Finally pour off the water as completely as possible. Add 5 cubic centimeters of nitric acid, boil to expel red fumes, add 1 or 2 drops of hydrochloric acid and 20 cubic centimeters of water. Filter and determine the copper in the filtrate by titration with standard potassium-cyanide solution, as previously described.

3. *The Iodide Method.*—Treat from .5 to 1 gram of the finely powdered ore in a flask of about 250 cubic centimeters capacity with 10 cubic centimeters of strong nitric acid, boil down to about 2 cubic centimeters, add 10 cubic centimeters of strong hydrochloric acid and boil for 3 minutes. Then add 10 cubic centimeters of strong sulphuric acid and boil until all the nitric and hydrochloric acids are expelled and dense fumes of SO_3 are evolved. When cool, add about 35 cubic centimeters of water, and boil. Filter through a small paper, catching the filtrate in a small beaker; wash the flask and insoluble residue with water, keeping the total volume of liquid down to about 75 cubic centimeters. Place in the beaker a piece of sheet aluminum about 2 inches square with the corners bent up at right angles about .5 inch, cover the beaker and boil until all the copper is precipitated. This will take about 10 minutes for 75 cubic centimeters of the liquid; a longer time is required when the liquid is more dilute. Pour the liquid into the flask and wash as much of the copper in with the liquid as possible. A very small

amount will stick to the aluminum. Fill the flask with water, allow the copper to settle, and decant the liquid through a small filter. Fill again with water and continue washing by decantation, pouring all the washings through the small paper until the copper is washed clean. Place the small beaker with the aluminum in it under the funnel and pour 4 cubic centimeters of strong nitric acid, drop by drop, on the paper. This will dissolve the small particles of copper that may have been carried over with the wash water, and, falling in the beaker, will dissolve the copper sticking to the aluminum. Wash with a few cubic centimeters of water. Make sure that all the copper in the beaker is dissolved, and transfer the acid to the flask containing the copper; use as little water as possible to rinse the beaker and aluminum. The same sheet of aluminum may be used for a number of determinations. Boil the liquid in the flask until red fumes cease to come off. Add .5 gram of $KClO_3$ and continue boiling until the volume of liquid is reduced to about 2 cubic centimeters, but do not heat enough to form insoluble basic salts. Add 5 cubic centimeters of water and 5 cubic centimeters of strong ammonia. Make sure that the copper is all in solution. Heat to boiling, and boil 1 minute. Add 6 cubic centimeters of strong acetic acid and 40 cubic centimeters of cold water. Make sure that the copper is all in solution and the liquid acid. Titrate with sodium thiosulphate, as previously described. Where a variety of ores are analyzed, some prefer the volumetric methods to the electrolytic. The cyanide method yields fairly good results and has the advantage of being very rapid. The iodide method yields very accurate results, and, while not so rapid as the cyanide method, is more rapid than the electrolytic.

ZINC

64. Zinc is practically always determined volumetrically by titration with potassium ferrocyanide. A qualitative analysis should always be made, as when cadmium and copper are present the treatment is somewhat different from

that when these metals are absent. In addition to the solutions mentioned under the Ferrocyanide Method for Zinc, two other solutions are needed for their determination.

1. *Potassium-Chlorate and Nitric-Acid Mixture.*—Make a cold saturated solution of $KClO_3$ in concentrate HNO_3. Put in a flask with several grams of $KClO_3$ to keep it saturated, and keep in a dark place covered with a small inverted beaker. It is not safe to keep this liquid in a tightly stoppered bottle.

2. *Washing Solution.*—Dissolve 10 grams of ammonium chloride in 1 liter of distilled water and add 10 cubic centimeters of strong ammonia.

65. Treatment of Ore.—Weigh 1 gram of the finely pulverized ore into a casserole, cover with a watch glass, add 12 cubic centimeters of concentrate HCl and 3 cubic centimeters of concentrate HNO_3. When the violent action ceases, evaporate over a flame (leaving the casserole covered) to about 3 cubic centimeters. Cool, add 25 cubic centimeters of the potassium-chlorate and nitric-acid mixture. Add this slowly, and when the violent action has ceased, heat over a free flame, leaving the casserole covered and keeping it in constant motion until the liquid has all evaporated. This requires great care, as there is danger of loss from spattering and it is necessary that all the acid be driven off, but the solid residue must not be overheated. Cool, add 7 grams of ammonium chloride, 15 cubic centimeters of strong ammonia, and 25 cubic centimeters of hot water. Boil for 1 minute and break up any clots with a glass rod. Filter through a large paper and wash with boiling washing solution. If a large precipitate is formed here, it is almost sure to carry part of the zinc. To remove this, transfer the precipitate back to the casserole, evaporate the water, and treat again with the potassium-chlorate and nitric-acid mixture. This is evaporated and treated as before and the two filtrates united. If the ore contains no copper or cadmium, the solution is treated as described under the Ferrocyanide Method for Zinc. If the ore contains copper, after just

neutralizing the ammoniacal solution with hydrochloric acid, add 30 grams of test lead and boil until all the copper is precipitated, or evaporate to a small bulk and precipitate the copper by boiling with aluminum. If cadmium is present, it may be removed with the copper by passing hydrogen sulphide through the slightly acid solution. In case hydrogen sulphide is used, it is not necessary to boil it from the filtrate from the cadmium and copper sulphides before proceeding with the determination.

LEAD

66. Lead may be determined both by gravimetric and volumetric methods. The gravimetric method is the more accurate; but it requires more time and more careful manipulation.

1. *Gravimetric Method.*—Treat 1 gram of the finely pulverized ore in a casserole with 15 cubic centimeters of strong nitric acid. Heat until the ore is decomposed and sulphur oxidized. Then add 10 cubic centimeters of dilute (1:1) sulphuric acid and boil until the nitric acid is driven off and fumes of SO_3 are evolved. Cool, dilute cautiously with about 50 cubic centimeters of water, break up any clots that have formed, and heat in order to dissolve any basic sulphate of iron that may have formed. Allow to cool, filter, and wash the residue with water containing about 1 per cent. of sulphuric acid, then with about 40 cubic centimeters of alcohol. Dissolve the lead sulphate with a hot solution of ammonium acetate made by acidifying strong ammonia with acetic acid. All the lead sulphate can generally be dissolved by three washings with the ammonium acetate. The lead in the ammonium-acetate solution is determined as sulphate, following the directions given under Soft Solder or Pewter.

2. *Volumetric Method.*—Treat from .5 to 1 gram of finely pulverized ore in a casserole with 15 cubic centimeters of concentrate nitric acid and 10 cubic centimeters of concentrate sulphuric acid. When ore is decomposed, carefully heat until all nitric acid is driven off and dense fumes of SO_3

appear. Allow to cool, dilute with cold water, and boil until all soluble sulphates are in solution. Filter, leaving as much of the precipitate in the casserole as possible, wash twice with hot 1-per-cent. sulphuric acid and once with cold water. Wash any precipitate on the paper back into the casserole, using a very small amount of water. Add 30 cubic centimeters of a saturated solution of ammonium carbonate, heat quickly to boiling, and boil for 1 minute in order to decompose any calcium sulphate that may have formed along with the lead sulphate—otherwise the calcium will react on the lead and cause low results. Filter, and wash the precipitate with hot water. Dissolve the washed lead carbonate in concentrate acetic acid, dilute to 180 cubic centimeters, heat to 80° C., and titrate with standard ferrocyanide.

A solution of ferrocyanide for this determination is made by dissolving about 14 grams of pure potassium ferrocyanide in 1 liter of distilled water. One cubic centimeter of this solution corresponds to about .01 gram of lead; but it must be standardized by dissolving weighed amounts (from .2 to .3 gram) of pure lead sulphate in hot ammonium acetate, diluting to 180 cubic centimeters, heating to 80° C., and titrating with the ferrocyanide, using uranium acetate as an indicator, in the same way as the titration for zinc is carried out.

QUANTITATIVE ANALYSIS

(PART 7)

GAS ANALYSIS

GENERAL PRINCIPLES

1. Although the principles underlying the various forms of gas analysis are themselves of a simple nature, the apparatus employed and the manipulative details involved are in some cases of a comparatively complicated and intricate nature. This is especially the case when the analysis is to be executed with that high degree of exactness essential to scientific research, and, until quite recently, these very exact but also very slow methods of gas analysis were also the only available ones for practical purposes. The growing demand of late years for simpler and more rapid methods, sufficiently accurate for technical purposes, has originated simpler and more rapid methods, and has led to the invention of various forms of gas apparatus, which not only yield good results, but also demand only a minimum amount of time, energy, and operative skill.

It is not within the scope of this Course to dwell upon the more complicated and delicate methods of gas analysis used in research work, but it is our aim to make the student familiar with the simpler and practical determinations he is most likely to be called on to perform.

2. Determination of Gases.—The methods by which gases are determined may be classified according to the following: (1) Absorption of the gas in a suitable reagent and subsequent titration; (2) absorption of the gas in a suitable reagent and subsequent measurement of the residual gas; (3) combustion of the gas, with the subsequent measurement of the contraction and estimation of the carbon dioxide, if any is formed

A few examples will serve to give the student a general idea of the principles of each of the above enumerated methods.

1. *By Absorption in a Suitable Reagent and Subsequent Titration.*—The carbon dioxide present in a gaseous mixture, as, for instance, air, may be determined by bringing a known volume of the gas into contact with an excess of a standard solution of barium hydrate. Barium carbonate is thereby precipitated, and the excess of barium hydrate is determined by titration with a standard solution of oxalic acid.

2. *By Absorbing the Gas in a Suitable Reagent and Subsequent Measurement of the Residual Gas.*—The carbon dioxide in a mixture of gases is determined by exposing a measured volume of the mixture to the action of potassium hydrate, and, after the whole of the carbon dioxide has been absorbed, the volume of the residual gas is measured. The difference, or the *contraction*, represents the carbon dioxide that was present.

3. *By Combustion of the Gas, with the Subsequent Measurement of the Contraction and Estimation of the Carbon Dioxide, if any is Formed.*—Hydrogen in a gaseous mixture may be estimated by adding to a known volume of the mixture a measured volume of oxygen or air more than sufficient to combine with all the hydrogen. These are caused to unite (by methods to be described later), and the contraction ascertained by again measuring the gas. Since 2 volumes of hydrogen and 1 volume of oxygen unite to form water (which practically occupies no volume), two-thirds of the contraction represents the hydrogen originally present. When the gas to be estimated contains carbon and hydrogen (as in

marsh gas, ethylene, etc.), after the contraction due to combustion has been measured, the volume of carbon dioxide produced is determined by absorption with potassium hydrate and measurement of the residue.

ESTIMATION OF GASES BY ABSORPTION AND SUBSEQUENT TITRATION

ESTIMATION OF CARBON DIOXIDE IN AIR

3. The most varied experience has shown that, through the process of breathing, the air acquires properties that cause it to act deleteriously on health when the products of breathing exceed a certain limit. Since we are not able, by ordinary means, to determine the other substances that are here formed, we make use of von Pettenkofer's suggestion and judge of the purity of the air by the percentage of carbon dioxide present. According to von Pettenkofer, the carbon dioxide in the air should not be raised, by breathing, to over .1 per cent.

The process best suited to the quantitative determination is that first used by Saussure and modified by von Pettenkofer, and generally known as **von Pettenkofer's methods.** The sample of air to be examined is contained in a large, wide-mouthed glass jar, the exact capacity of which is known, and that can be closed with an air-tight fitting rubber stopper. The temperature of the air and the atmospheric pressure are noted at the time the sample is taken. A measured volume of a solution of barium hydrate of known strength is introduced into the jar, and thoroughly shaken up with the enclosed air until the carbon dioxide is all absorbed. Aliquot portions of the liquid are then withdrawn, and titrated with a solution of oxalic acid of known strength.

4. Standard Oxalic Acid.—In order to simplify the subsequent calculations, the strength of the oxalic-acid solution

may be made up so that 1 cubic centimeter is equivalent to 1 cubic centimeter carbon dioxide measured under standard conditions, that is to say, 1 cubic centimeter of the acid is capable of saturating a quantity of barium hydrate that would be decomposed by this volume of carbon dioxide, the weight of which is .00197 gram. Oxalic acid of this strength would contain 5.6414 grams of the crystallized acid $H_2C_2O_4 \cdot 2H_2O$ in 1 liter; but, as dilute solutions of oxalic acid are not stable, it is advisable to prepare a solution that contains 56.414 grams of $H_2C_2O_4 \cdot 2H_2O$ per liter, and to withdraw an aliquot proportion and dilute it whenever required. Thus, 56.414 grams of dry, crystallized oxalic acid are exactly weighed out, dissolved in cold, air-free water (that is, distilled water that has been recently boiled to expel all carbon dioxide, and quickly cooled), and the solution made up to 1 liter. For use, 10 cubic centimeters are transferred to a 100-cubic-centimeter flask by means of a pipette, and the solution diluted to 100 cubic centimeters with air-free water.

5. Barium-Hydrate Solution.—Place 40 to 50 grams of crystallized barium hydrate $Ba(OH)_2 \cdot 8H_2O$, powdered or crushed, in a large glass-stoppered bottle, and add 1 liter of water. The mixture is thoroughly shaken from time to time, until the water is saturated, after which it is allowed to settle. The clear liquid is carefully decanted or filtered into another glass-stoppered bottle, and diluted with an equal volume of water. This solution will possess approximately the same relative strength as that of the oxalic acid previously mentioned. A solution of exact equivalent strength, of which 1 cubic centimeter = .00197 gram CO_2 (i. e., 1 cubic centimeter CO_2 at normal temperature and pressure), would contain 14.11 grams of $Ba(OH)_2 \cdot 8H_2O$ per liter. Such a solution cannot be obtained by direct weighing, as, the salt being efflorescent, its state of hydration is uncertain; and it also absorbs atmospheric carbon dioxide. A saturated solution at the ordinary temperature contains about 32 grams per liter; hence, if this be diluted with its

own volume of water, the solution, as first prepared, will contain about 16 grams per liter. As the solution constantly undergoes change by the absorption of atmospheric carbon dioxide, its value must be determined every time before it is used by titration against the standard oxalic acid. The stopper of the bottle containing the barium-hydrate solution should be greased, so as to exclude the air as much as possible.

6. Standardizing the Barium-Hydrate Solution.—In a small flask are placed 20 cubic centimeters of standard oxalic acid and then 25 cubic centimeters of the barium-hydrate solution added. The solution is then neutralized by slowly running in more oxalic acid by means of a burette until the liquid ceases to give any indication of a brown color when a drop of it is placed on a piece of turmeric paper. The alkali is gradually neutralized by the oxalic acid; the brown color, which at first is very evident, gradually shows more and more as a faint fringe of color round the edge of the moistened spot on the turmeric paper, until finally it disappears. Suppose, for instance, that 28 cubic centimeters of the oxalic acid are used; then, 100 cubic centimeters of this barium-hydrate solution would require 112 cubic centimeters of the oxalic acid to exactly neutralize it.

7. Determination of Carbon Dioxide.—A large glass jar, whose mouth is sufficiently wide to admit the hand, so that it may be conveniently wiped dry inside with a cloth, is fitted with a rubber stopper. A hole is bored in the stopper, and this hole is closed with a piece of glass rod. The capacity of the jar is ascertained by filling it with water up to the stopper, and measuring the volume of the water. As it is evident that when the amount of carbon dioxide present is small, the accuracy of the determination is increased by using larger volumes of air; it is advisable that the jar should hold from 8 to 10 liters, if possible, but not less than 5 liters. Its exact capacity should be scratched on the vessel.

The jar is filled with the air to be tested by leading into it, right to the bottom of the jar, a piece of rubber tubing attached to a pair of bellows and blowing a stream of air for about 5 to 6 minutes, in order to insure complete displacement of the air already in the vessel. The stopper is then inserted. The temperature of the air in the immediate vicinity of the jar is noted, and also the height of the barometer at the same time. By means of a pipette, 100 cubic centimeters of the barium-hydrate solution are then delivered in the jar through the hole in the stopper, and the glass rod is immediately replaced. The liquid is then made to wet the surface of the glass by slowly revolving the vessel upon its side; and it is left in contact with the gas, being shaken at intervals for about 30 to 40 minutes, by which time all the carbon dioxide will have been absorbed. When the absorption of the carbon dioxide is complete, 25 cubic centimeters of the turbid liquid are withdrawn by means of a pipette, to which a piece of glass tubing has been attached in order that the bottom of the jar may be reached. This arrangement is introduced through the hole in the rubber stopper, as shown in Fig. 1. When the pipette is full, the piece of rubber is detached, and the liquid allowed to drip from the pipette until it reaches the graduation mark. The measured volume is then transferred to a beaker, and immediately titrated with oxalic acid, exposure to the air being avoided as much as possible. The end of the reaction is indicated by means of turmeric paper, used as described in Art. **6.** A duplicate titration should be made with a second portion of the liquid. Some chemists prefer to use a solution of phenol phthalein in alcohol as an indicator. In this case, about 2 cubic centimeters of this indicator are added to the liquid, and the

FIG. 1

oxalic acid added until the liquid becomes neutral, which is indicated by the disappearance of the color.

Since 25 cubic centimeters (out of the 100 cubic centimeters of the barium-hydrate solution originally placed in the jar) have been used for titration, the volume of oxalic acid used, multiplied by 4, will give the amount of oxalic acid required to neutralize the 100 cubic centimeters of the barium-hydrate solution after the absorption of the carbon dioxide in the known volume of air. This, obviously, will be less than that required by 100 cubic centimeters of the original barium-hydrate solution by just the volume of carbon dioxide that was contained in the sample of the air.

The following details of an analysis will make this determination perfectly understood:

Capacity of glass jar	=	10.5 liters
Temperature of the air	=	17°
Barometer reading	=	769 mm.

Then, $$\frac{10.5 \times 273 \times 769}{(273+17) \times 760} = 10.001 \text{ liters,}$$

which is equal to the volume of the sample at normal temperature and pressure.

The value of the barium-hydrate solution is 100 c. c. = 112 c. c. of the standard oxalic-acid solution; 100 c. c. of the barium hydrate were used for absorption; 25 c. c. were taken out for titration; 25 c. c. required 27.10 c. c. of standard oxalic acid; therefore, 100 c. c. would require $27.10 \times 4 = 108.4$ c. c. oxalic acid. $112 - 108.4 = 3.6$ c. c. = the volume of oxalic acid, which is equivalent to the carbon dioxide absorbed by the 100 c. c. of barium-hydrate solution.

But, since 1 c. c. of oxalic acid = 1 c. c. CO_2 at normal temperature and pressure, 3.6 c. c. oxalic acid = 3.6 c. c. CO_2 present in 10.001 liters or 10,001 c. c. of air.

Therefore, $$\frac{3.6 \times 100}{10{,}001} = .0359 = \text{percentage of } CO_2 \text{ by volume}$$

8. Since the presence of barium carbonate does not interfere with the titration, some chemists prefer to titrate

directly in the same vessel in which the air has been collected. This method has the advantage that the barium-hydrate solution is the least exposed to air. For this purpose, a liter flask is employed, which is fitted with a rubber stopper having two perforations that are closed with pieces of glass rod. After sampling the air and adding 10 cubic centimeters of barium-hydrate solution, the burette containing the standard oxalic acid is inserted into one of the perforations, as shown in Fig. 2, and the titration carried out as previously described. As an indicator, about 1 cubic centimeter of phenol phthalein in alcohol is used. The titration is finished as soon as the last trace of color disappears. If the increased pressure resulting inside the flask checks the flow of the liquid from the burette, this pressure is removed by lifting the glass stopper closing the second perforation. The only disadvantage of this method is that but a comparatively small volume of air can be used.

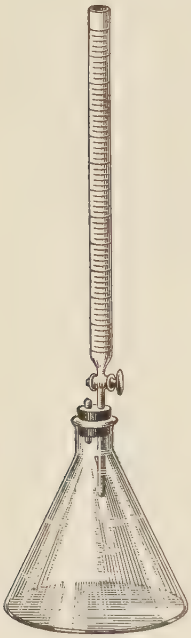

FIG. 2

ESTIMATION OF SULPHUR DIOXIDE IN FURNACE GASES

9. By means of a pipe inserted into the flue, a measured volume of the furnace gases is aspirated, with a suitable aspirator, through a known volume of a dilute standard solution of iodine, and the excess of iodine titrated with a standard solution of sodium thiosulphate.

10. Standard Iodine Solution.—Pure resublimed iodine to the amount of 12.7 grams, is powdered and weighed out into a liter flask. About 20 grams of potassium iodide (free from iodate), dissolved in 100 cubic centimeters of water, are added, and the mixture gently shaken until the

iodine is entirely dissolved. The solution is then diluted up to the liter with water at 15° and preserved in a well-fitting stoppered bottle in the dark; 1 cubic centimeter of this solution will contain .0127 gram of iodine, and is equivalent to .0032 gram of SO_2. It is, however, more convenient in this case and simplifies the calculation, to employ solutions of such strength that 1 cubic centimeter shall equal 1 cubic centimeter SO_2 measured at normal temperature and pressure, i. e., .002867 gram SO_2 instead of .0032. Such a solution will contain 11.379 grams of iodine per liter, and may be most conveniently obtained by diluting 100 cubic centimeters of the above solution to 111.6 cubic centimeters. In case the percentage of SO_2 in the gas under examination is comparatively small, it is better to employ a solution of one-tenth this strength, in which 1 cubic centimeter = .1 cubic centimeter SO_2.

11. Standard Sodium-Thiosulphate Solution.—To obtain a standard solution, 1 cubic centimeter of which is equivalent to 1 cubic centimeter SO_2, i. e., .002867 gram SO_2, 22.22 grams of sodium thiosulphate $Na_2S_2O_3 \cdot 5H_2O$, which has been carefully powdered, are weighed out into a liter flask and dissolved in water. The solution is then diluted to the 1,000-cubic-centimeter mark with water at 15°. If 100 cubic centimeters of this solution are again diluted to 1,000 cubic centimeters, each cubic centimeter is equivalent to .1 cubic centimeter SO_2. As it is practically impossible to obtain sodium thiosulphate containing exactly the theoretical amount of water of crystallization, it is preferable to weigh out about 23 grams of the salt, and titrate it against the iodine solution of known strength, and from the results, calculate the amount of water that has to be added to make 1 cubic centimeter equivalent to exactly 1 cubic centimeter of the iodine solution.

12. Starch Solution.—The starch solution, serving as an indicator, is prepared by mixing 1 or 2 grams of dry starch in a medium-sized beaker with 5 or 6 cubic

centimeters of cold water. A considerable quantity of boiling water is then poured on it. As the hot water is being added, the opaque white appearance, which the mixture presents at first, changes almost suddenly to that of a semi-translucent gelatinous substance. At this point, the addition of the boiling water is stopped, and the beaker nearly filled up with cold water. It is allowed to settle, and the clear liquid poured off for use. This starch solution should be made up fresh every time, as it will not keep more than a day.

13. Determination of Sulphur Dioxide.—The apparatus used in this determination is known as **Reich's apparatus**; it consists of a double-necked absorption bottle *a*, the aspirator *b*, and the glass cylinder *e*. These are supported by a convenient stand, as shown in Fig. 3. The rubber tube joining *a* and *b* is about 30 centimeters long; 100 cubic centimeters of the $\frac{n}{100}$ iodine solution are placed in the bottle *a*, and the aspirator *b* is filled with water. Before making a determination, the air in the tubes leading to the apparatus is displaced by the gas to be examined. The apparatus is tight if, after a short time and as soon as the air in *a* is correspondingly expanded, the water ceases entirely to flow from the aspirator. In making the determination, the stop-cock *c* is opened, and the amount of water that is necessary to draw over sufficient gas to decolorize the iodine solution is measured in the cylinder *e*. During the determination, the bottle *a* is frequently shaken. The volume of water that has run out is equal to that of the gas taken, and the quantity of sulphur dioxide

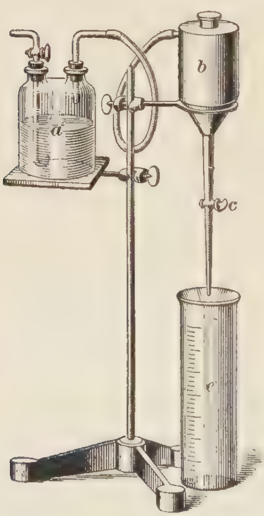

FIG. 3

can approximately be told from the amount of iodine used. During the experiment, the temperature of the water is taken (which will be the temperature of the gas) and the height of the barometer is noted.

When 8 or 10 liters* of gas have in this way been aspirated through the iodine solution, the process is stopped, and 25 cubic centimeters of the iodine solution are transferred to a beaker and titrated with the standard sodium thiosulphate. As soon as the red-brown color of the iodine solution changes to a straw color, 1 or 2 drops of dilute starch solution are added, and the titration continued, drop by drop, until the blue color is entirely discharged. A duplicate titration is made in a second portion of the solution.

The following record of an analysis will make this determination more clear.

Gas drawn from the flue of a coke furnace:

Volume of water drawn from aspirator	= 8.25 liters
Temperature	= 16°
Atmospheric pressure	= 765 mm.

Volume of gas operated upon equals

$$\frac{(8.25 \times 273) \times 765}{(273 + 16) \times 760} = 7.8445 \text{ liters}$$

at normal temperature and pressure.

100 c. c. of iodine solution are employed in the absorption flask.

1 c. c. = 1 c. c. of thiosulphate = .1 c. c. SO_2 at normal temperature and pressure.

After absorption, 25 c. c. of iodine solution required 18.2 c. c. sodium thiosulphate.

* When the gas is very rich in sulphur dioxide, as, for instance, in the flue gases from the sulphur burner in vitriol works, a much smaller volume, say 1 liter, need be drawn through the apparatus, and, in the final correction of the volume of gas operated on, the volume of sulphur dioxide that has been absorbed must be added to the volume of water measured out of the aspirator. In the example here given, where the amount of sulphur dioxide is small, these corrections are left out, as they would not affect the third decimal figure.

Volume of thiosulphate required for 100 c. c. = 18.2×4 = 72.8 c. c., and volume of SO_2 absorbed equals

$$\frac{100 - 72.8}{10} = 2.72 \text{ c. c.}$$

Hence, 7,844.5 c. c. of the furnace gas contain 2.72 c. c. SO_2, or

$$\frac{2.72 \times 100}{7{,}844.5} = .0346 \text{ percentage } SO_2 \text{ by volume}$$

ESTIMATION BY ABSORPTION AND MEASUREMENT OF RESIDUAL GAS

14. The processes employed by this method differ from the foregoing, in that they involve (1) manipulation of comparatively small volumes of gas, and (2) the accurate measurement of these volumes.

For the manipulation of small volumes of gas, special apparatus is required; and for the accurate measurement of gaseous volumes, special precautions are necessary.

15. Simple Gas Burette.—The simple gas burette, which is shown in Fig. 4, consists of two glass tubes *a* and *b*, which are set in iron feet and are connected by a thin rubber tube about 120 centimeters long. To facilitate the cleaning of the burettes, the rubber tube is cut in two parts, and the two ends joined by a piece of glass tubing. Inside the feet, the tubes *a* and *b* are bent at right angles and conically drawn out. The end projecting from the iron is about 4 millimeters external diameter, and is somewhat corrugated, so that the rubber can be tightly fastened to it by winding it with thin wire. The measuring tube *b* ends at the top in a thick-walled tube *c* of from $\frac{1}{2}$ to 1 millimeter internal diameter, and about 3 centimeters long. Over this, a short piece of new, black, rubber tubing *d* is wired on. The rubber tube is closed by a Mohr pinch cock *f*, which is put on close to the end of the capillary. The graduated measuring tube *b* holds 100 cubic centimeters, the lowest mark being slightly above the iron foot. The cubic centimeters are divided into fifths, and the

graduation runs up and down. The tube *a*, generally known as the level tube, is somewhat widened at the upper end, to facilitate the pouring in of liquids.

16. Manipulation of the Gas Burette. Fill the tubes *a* and *b*, Fig. 4, with water, taking care to drive all the air out of the connecting rubber tube by either raising or lowering the tubes; then join the burette to the vessel containing the gas by means of a glass or rubber tube filled with water. This connecting tube can be easily filled with water by raising the level tube.

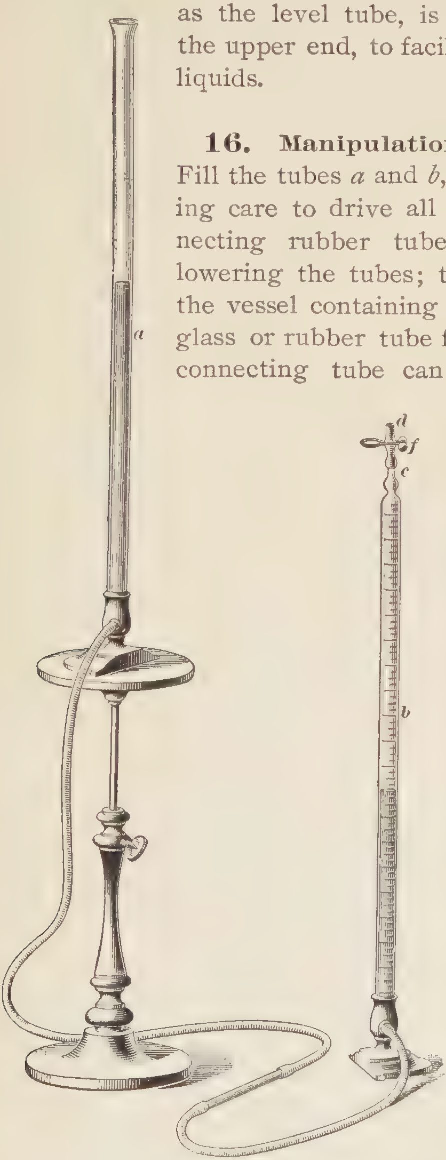

FIG. 4

To fill the burette with the gas to be examined, grasp the tube *a* in the left hand, close the rubber tube by pressing it between the little finger and the palm of the hand, and pour out the water in *a*. Place the level tube on the floor and open the pinch cock *f*. The water will now flow into the level tube and the gas will be drawn into the burette. When *b* is filled with the gas, close the pinch cock *f*, disconnect *b* from the gas holder, and, after the liquid has run down

from the walls of the burette, take up the tubes by the iron feet and, by raising or lowering, bring the water in the tubes to the same level. The gas is now under atmospheric pressure and its volume is read off. To measure off exactly 100 cubic centimeters, bring somewhat more than 100 cubic centimeters of the gas into the burette, close the latter with the pinch cock, and allow the water to run down the walls of the burette. Now compress the gas to a little less than 100 cubic centimeters by raising the level tube, close the rubber tube with the thumb and first finger of the left hand, set the level tube on the table, and, raising the burette with the right hand to the level of the eye, carefully open the rubber tube and let the water run back until the meniscus stands at the 100-cubic-centimeter mark. Keeping the rubber still compressed, open the pinch cock for a moment. The excess of the gas will escape, and there remains in the burette exactly 100 cubic centimeters of gas under atmospheric pressure.

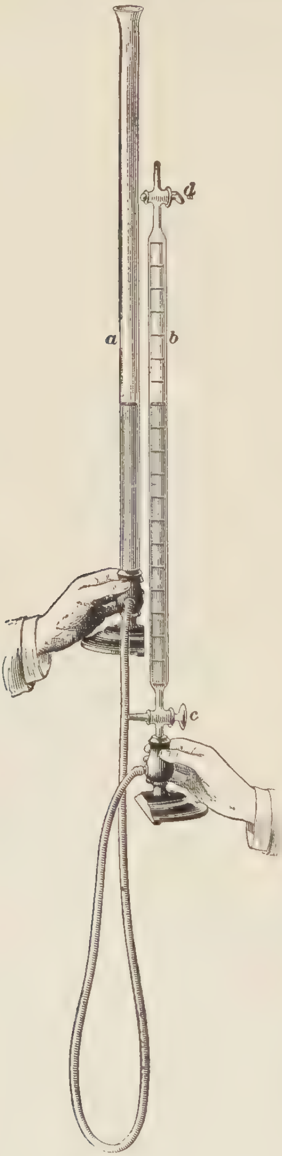

FIG. 5

17. Modified Winkler Gas Burette.—The modified Winkler gas burette shown in Fig. 5 consists of the level tube *a* and the measuring tube *b* connected by a thin rubber tube about 120 centi-

meters long. The glass tube *b* is about 100 cubic centimeters capacity, provided with the simple glass stop-cock *d*, and the three-way stop-cock *c*, which allows of communication being established with the level tube or with the outer air at will. This will be seen more clearly in Fig. 6. The space between the two stop-cocks is divided into exactly 100 equal parts, with subdivisions of one-fifth cubic centimeter each, and the graduations are numbered in both directions. The thick-walled tube (Fig. 5) must have a diameter of from only $\frac{1}{2}$ to 1 millimeter, so that bubbles of the gases that are passed in and out cannot stop in this tube. The manipulation of the burette is practically the same as that described in the preceding article.

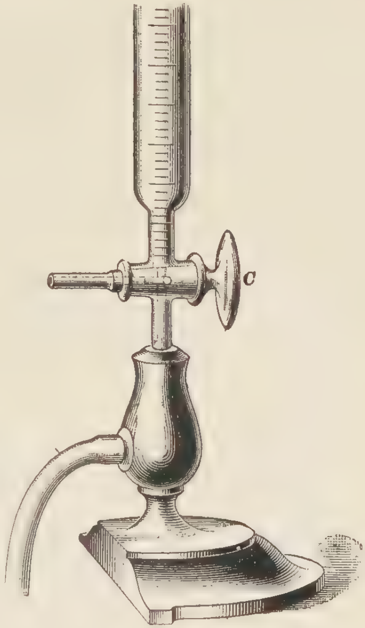

FIG. 6

18. Correction of Gaseous Volume.—The volume of gas has been briefly treated in sections on *Physics* and *Inorganic Chemistry*, but a short repetition and expansion of the subject appears appropriate here. It has been stated in the sections mentioned, that the volume of a given weight of a gas depends on the pressure and the temperature; in gas analysis, however, a third factor has to be taken into account, namely, the degree of humidity of the gas at the time the measurement is made.

In order, therefore, that the various volumes observed during an analysis shall be comparable with one another, it is necessary either that the conditions mentioned should remain constant throughout, or that the volumes measured

under different conditions should be reduced by calculation to one common standard.

In exact methods of analysis, the latter plan is invariably adopted, but in the more rapid and somewhat rougher methods employed for technical purposes, the analysis may usually be carried out without disturbing the uniformity of conditions to an extent that will introduce any material error in the results. The recognized standard to which gaseous volumes are reduced is the volume that the gas would occupy at 0° and under a pressure of 760 millimeters, *when in the dry state.*

19. Correction of Temperature.—The coefficient of expansion is usually taken as $\frac{1}{273}$, or .003665; therefore, the volume at 0° equals the volume at t° divided by $1 + .003665\,t$. Hence,

$$V_0 = \frac{V}{1 + .003665\,t} \text{ or } \frac{V \times 273}{273 + t} \qquad (1)$$

where V_0 = volume at 0°, and V = volume at t°.

20. Correction of Pressure.—According to Mariotte's law, quoted in previous Sections, the volume of a gas being inversely as the pressure,

$$V_0 = \frac{VP}{760} \qquad (2)$$

where V = volume at P pressure; or, making the corrections for temperature and pressure together, we obtain the formula

$$V_0 = \frac{VP}{760(1 + .003665\,t)} \text{ or } \frac{VP \times 273}{760 \times (273 + t)} \qquad (3)$$

21. Correction for Tension of Aqueous Vapor.—The aqueous vapor present in a gas exerts a pressure in opposition to the barometric pressure; hence, the volume of gas is increased by the presence of aqueous vapor. If the gas is saturated with aqueous vapor, and an excess of water, however indefinitely small, is present, then the pressure or tension of the aqueous vapor is independent of change of pressure, varying only with change of temperature. The *tension of aqueous vapor* has been experimentally determined for every degree of temperature, and in Table I will be found the tension or pressure, in millimeters of mercury, of the vapor of water between the temperatures 5° and 30°

TABLE I

TENSION OF AQUEOUS VAPOR IN MILLIMETERS OF MERCURY FOR EACH FIFTH OF A DEGREE FROM 5° TO 30°

C°.	t mm.	C°.	t mm.	C°.	t mm.	C°.	t mm.	C°.	t mm.
5.0	6.5	10.0	9.2	15.0	12.7	20.0	17.4	25.0	23.5
.2	6.6	.2	9.3	.2	12.9	.2	17.6	.2	23.8
.4	6.7	.4	9.4	.4	13.0	.4	17.8	.4	24.1
.6	6.8	.6	9.5	.6	13.2	.6	18.0	.6	24.4
.8	6.9	.8	9.7	.8	13.4	.8	18.3	.8	24.7
6.0	7.0	11.0	9.8	16.0	13.5	21.0	18.5	26.0	25.0
.2	7.1	.2	9.9	.2	13.7	.2	18.7	.2	25.3
.4	7.2	.4	10.1	.4	13.9	.4	19.0	.4	25.6
.6	7.3	.6	10.2	.6	14.1	.6	19.2	.6	25.9
.8	7.4	.8	10.3	.8	14.2	.8	19.4	.8	26.2
7.0	7.5	12.0	10.5	17.0	14.4	22.0	19.7	27.0	26.5
.2	7.6	.2	10.6	.2	14.6	.2	19.9	.2	26.8
.4	7.7	.4	10.7	.4	14.8	.4	20.1	.4	27.1
.6	7.8	.6	10.9	.6	15.0	.6	20.4	.6	27.4
.8	7.9	.8	11.0	.8	15.2	.8	20.6	.8	27.7
8.0	8.0	13.0	11.2	18.0	15.4	23.0	20.9	28.0	28.1
.2	8.1	.2	11.3	.2	15.6	.2	21.1	.2	28.4
.4	8.2	.4	11.5	.4	15.7	.4	21.4	.4	28.7
.6	8.3	.6	11.6	.6	15.9	.6	21.7	.6	29.1
.8	8.5	.8	11.8	.8	16.1	.8	21.9	.8	29.4
9.0	8.6	14.0	11.9	19.0	16.3	24.0	22.2	29.0	29.7
.2	8.7	.2	12.1	.2	16.6	.2	22.5	.2	30.1
.4	8.8	.4	12.2	.4	16.8	.4	22.7	.4	30.4
.6	8.9	.6	12.4	.6	17.0	.6	23.0	.6	30.8
.8	9.0	.8	12.5	.8	17.2	.8	23.3	.8	31.1
								30.0	31.5

NOTE.—In cases where the tension rises .1 millimeter for a rise of .2°, the same pressure for the intermediate tenth degree may be taken as that given for the temperature immediately preceding it. Thus, for the temperature 10.1°, the tension 9.2 millimeters will be taken. For very accurate work, fuller tables given to the third decimal should be consulted.

In making the necessary correction for aqueousvapor, therefore, the number of millimeters of mercury representing the tension of aqueous vapor at that particular temperature at which the gas is measured, is deducted from the barometric pressure to which the gas is exposed. For

example, a gas is measured at 763 millimeters, and the temperature is 13.4°; then, by referring to Table I, the tension at 13.4° is seen to be 11.5 millimeters. Deducting this from the barometric pressure, we obtain $763 - 11.5 = 751.5$ millimeters of true pressure.

If p stands for the pressure due to aqueous vapor, then the formula

$$V_0 = \frac{V(P-p)}{760(1+.003665\,t)}, \text{ or } \frac{V(P-p)\times 273}{760\times(273+t)} \qquad \textbf{(4)}$$

expresses the necessary corrections to reduce a volume of gas, saturated with aqueous vapor, to the standard conditions.

22. When gases are confined over water, as in the gas burettes just described, the conditions of complete saturation with aqueous vapor are, of course, always present, and when mercury is employed as the confining liquid, complete saturation of the gas with aqueous vapor is insured by introducing a drop of water into the measuring tube. With this apparatus also, the gas volumes are always read at the atmospheric pressure, and, as the analytical operations are rapidly performed, changes of barometic pressure sufficient to influence the results need not be anticipated. Changes of temperature, however, must be guarded against as far as possible, and, with this object in view, it should be made an imperative rule never to handle the glass parts of gas analytical apparatus. In order to ascertain the temperature of the gas and see how far it is being maintained uniform throughout, a simple and convenient plan is to suspend a thermometer inside the level tube by means of a thread, so that it reaches nearly to the bottom, and remains there during the whole analysis. As the water is continually being passed backwards and forwards from the level tube to the measuring tube, the temperature of the gas may be taken as the same as that of the water over which it is confined, and, if the temperature of the latter does not materially change, that of the gas may be considered as practically uniform.

23. As previously stated, when conditions under which gas measurements are made are constant, it is not necessary

to reduce the observed volume to the standard conditions. This will be rendered more obvious from the following example:

The original volume of gaseous mixture in the burette measured 100 cubic centimeters at ordinary pressure (i. e., when the water was at the same level in both tubes). One constituent x was then removed by absorption and the gas measured again. Its volume now was 75 cubic centimeters at atmospheric pressure. The temperature was 16° and the barometric pressure 758 millimeters throughout.

Then (1) without making reduction to standard conditions, we obtain

$$100-75 = 25 = \text{percentage of } x \text{ in the mixture}$$

(2) On reducing the two volumes by means of formula **4**,

$$V_0 = \frac{V(P-p)}{760(1+.003665\,t)},$$

we obtain

$$(a)\ V_0 = \frac{100\times(758-13.5)}{760\times(1.05864)} = 92.534$$

$$(b)\ V_0 = \frac{75\times(758-13.5)}{760\times(1.05864)} = 69.276$$

Therefore, $92.534-69.276 = 23.258$ = volume of x in 92.534 cubic centimeters of original gas, and

$$\frac{23.258\times 100}{92.534} = 25 = \text{percentage of } x \text{ in the mixture}$$

Since the tension of aqueous vapor is independent of pressure, then, in the event of any alteration of barometric pressure taking place during an analysis, it is only necessary to make a correction for pressure—not necessarily by reducing all the volumes to the standard, but by reducing all to the same pressure as any of them.

Thus, in the above, suppose that between the two measurements the barometer fell from 758 to 752 millimeters, the temperature remaining constant at 16°, then the following are the data:

Original volume = 100 c.c. at 16° and 758 mm.

After absorbing x, volume = 75 c.c. at 16° and 752 mm.

Then, $\frac{75 \times 752}{758} = 74.41$ = volume that the residual gas would occupy if measured under the same conditions as the original volume.

Hence, $100 - 74.41 = 25.59$ = percentage of x in the mixture.

If, now, from the above data, the two volumes be reduced to standard conditions by means of formula **4**, it will be found that the same result is obtained, namely, 25.59 percentage of x.

Again, since the tension of aqueous vapor depends on the temperature, increasing with the rise of temperature, change of temperature will obviously produce an alteration of the pressure, even though the barometric pressure remains constant. For example, suppose, in the above illustration, the 100 cubic centimeters of original volume are measured at 16° and the 75 cubic centimeters of residual gas are measured at 20°, the barometer standing uniformly at 760 millimeters, then the actual pressure in the first case is 760 − 13.5 (tension of aqueous vapor at 16°), and in the second it is 760 − 17.4 (tension at 20°).

Hence, if any change of temperature is observed in the gas during the progress of an analysis, the observed volumes must be reduced to the standard by means of formula **4**,

$$V_0 = \frac{V(P-p)}{760(1+.003665\,t)}$$

24. Collection of Gas for Analysis.—If the gas for analysis is collected in the laboratory, as, for instance, a sample of ordinary illuminating gas, it may be introduced into the burette by first placing the measuring tube on a higher level than the level tube, and allowing the former to empty. By means of the three-way cock, shown in Figs. 5 and 6, communication between the measuring tube and the outer air is then opened, and a rapid stream of the gas passed through the tube from the top, until the air has been entirely swept

out. The upper tap is then closed and the lower one turned so as to reestablish communication with the level tube.

When the available supply of gas is comparatively small, it may be collected in a glass tube over water (or, if necessary, over mercury), and afterwards transferred to the burette, as described below. The tube may conveniently have the form shown in Fig. 7. It is first filled with water by sucking the liquid up and closing the rubber tube with a pinch cock, and the gas is then passed up from below in the usual manner. The tube is then connected to the gas burette, with the same precautions against enclosing air in the joints, as given below. When the gas is collected away from the laboratory, it should be taken in glass tubes drawn out to a capillary constriction at each end. These tubes are filled either by aspirating the gas through them so as to sweep out the air, and then hermetically sealing them at the constriction, or by taking them to the spot in a vacuous and sealed condition, and then breaking open one end in the gas to be collected. After the gas has filled the tube, the end is again hermetically sealed by means of a blowpipe.

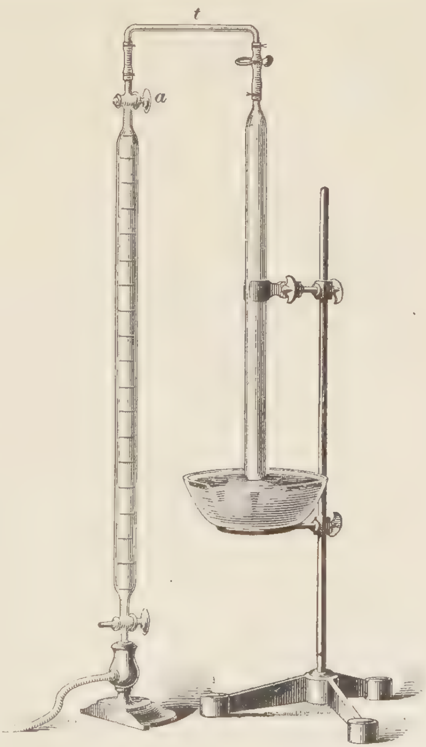

FIG. 7

In order to transfer the gas from the sealed tube to the burette, a piece of capillary tube t, bent twice in right angles, is attached to the latter, as shown in Fig. 7, the joints

being wired round. The level tube is then raised, until water completely fills the measuring tube and drops from the open end of the bent capillary. Whenever the available supply of the gas to be analyzed renders such a course possible, the water used in the burette should be first saturated with the gas by shaking a quantity of water with some of the gas in a stoppered bottle for a few minutes. Near each end of the sealed tubes, a slight scratch with a file is made. Over one end, a short piece of rubber tube is slipped, and the projecting portion of it filled up with water. The bent capillary, already entirely filled with water, is then introduced into this tube, and the latter secured with binding wire. In this way, all air is excluded from the joint. The lower end of the tube is dipped into a vessel of water. The tube is broken at the file mark within the rubber joint, and the end beneath the water is also broken off by means of a pair of pliers. On lowering the level tube and opening the stop-cock *a* at the top of the measuring tube, the gas will be drawn over into the burette.

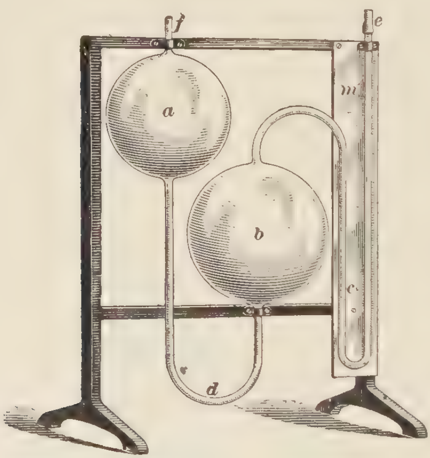

FIG. 8

25. Absorption of Gases. — Except when the absorbing liquid is water, in which case the absorption would be made directly in the measuring tube of the burette, the absorption of the gases in a mixture is carried out in a separate piece of apparatus known as *absorption pipette*. The *simple absorption pipette* shown in Fig. 8 consists of two glass globes *a* and *b*; the capacity of *b* should be at least 150 cubic centimeters, so that when the gas from the full burette (100 cubic centimeters) is transferred to it, sufficient room remains for

an adequate quantity of the reagent. The two globes are connected by means of a bent glass tube *d*, and are fastened to a wooden stand to prevent breakage. A capillary tube *c* passes from the globe *b* before a plate of milk glass *m*, which is let into the wooden stand, in order to be able to trace readily the movements of the liquid thread in the capillary tube *c*. The exit tube *f* of the globe *a* and capillary tube *c* extend above the wooden frame; a small rubber tube *e* is connected to the protruding tube *c* and fastened by means of wire, and the tube furnished with a pinch cock. The reagent to be used is poured in at *f* (for which purpose a thistle funnel should be used to avoid spilling the reagent over the outside), filling the globe *b* entirely, *a* only partially, and the capillary tube *c* to the junction with the rubber tube near *e*. When not in use, *f* is closed by a cork and *c* by a glass rod, not with the pinch cock, which spoils the rubber tube after a short time. A separate pipette is used for each reagent, and a label designating the contents of the pipette should be attached to the wooden frame of each.

26. Manipulation of Single-Absorption Pipette. To analyze a gas with the single-absorption pipette, the burette is filled with distilled water that has been previously saturated by shaking with the gas in question. The pipette is so filled with the absorbent that the bulb *a*, Fig. 8, remains empty. The absorbent must also be saturated, by shaking with gases that are but slightly soluble in it. The saturation of liquids is best done in a flask half filled with the reagent, a rapid stream of gas being led through the liquid, and the flask vigorously shaken. In technical work, where the same analyses are repeatedly made, the absorbent is kept saturated through continual use.

If the pipettes have the temperature of the room, as can be readily determined by introducing a thermometer at *k*, Fig. 9, the analysis is begun by drawing gas into the measuring tube in the manner described in Art. **16.** It is convenient to use exactly 100 cubic centimeters, so that the results in percentage may be read off directly. The

apparatus is now arranged as shown in Fig. 9. The pipette is placed on a wooden stand and is connected with the burette by the capillary tube F, which is a piece of ther-

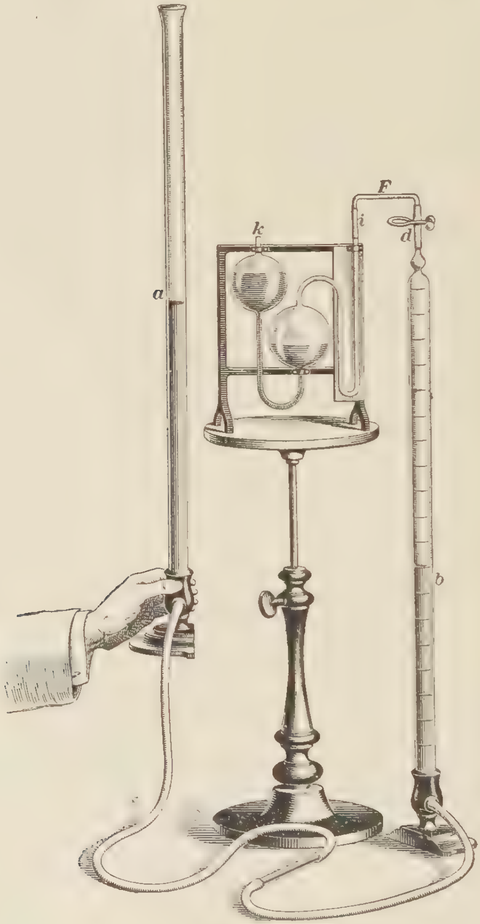

FIG. 9

mometer tubing having a bore of .5 millimeter. To avoid the enclosing of air bubbles, the rubber tube d is first filled with water by means of a funnel, and the capillary F is then introduced. F is thus completely filled with water. The

rubber tube *i* of the pipette is squeezed between the thumb and the first finger of the right hand, and, while thus compressed and free from air, the capillary connecting tube is inserted. On raising the level tube *a* and opening the pinch cock at *d*, the gas passes through the connecting tube into the absorption pipette. Any small air bubbles that may have been enclosed when *F* was inserted into *i* are, at the beginning, separated from the gas by the water in *F*. If these bubbles do not take more than 5 to 10 millimeters of space in the capillary of the pipette, they may be disregarded, since the error arising therefrom is only about .03 cubic centimeter.

If the bubbles are larger, although after a little practice this will seldom occur, the gas is brought back into the burette by lowering the level tube, and the operation is repeated. When the gas has passed over into the pipette, about ½ cubic centimeter of water is allowed to follow, this water serving to rinse the capillary and to free it sufficiently from the absorbing liquid that it previously contained. The gas is now enclosed between two columns of liquid, the absorbent on the one side and the water in the capillary on the other side. The burette, having been closed by the pinch cock, is disconnected, and the pipette is carefully shaken and the absorption of the gas thus effected. The burette and pipette are then reconnected, the level tube is placed on the floor, and the gas is brought back into the burette, care being taken that *none* of the absorbing liquid passes further than the connecting capillary *F*. The pinch cock is closed, and the reading of the remaining volume is made.

27. Double, or Compound, Pipette.—In cases where it is necessary to prevent the reagent from coming into contact with atmospheric air (as, for instance, with alkaline pyrogallol, cuprous chloride, etc.), the *double*, or *compound*, *pipette*, shown in Fig. 10, is used. It differs from the pipette shown in Fig. 8, by having two extra bulbs, which, being partially filled with water, serve as a water seal and thus

prevent the reagent from coming in contact with the air. The apparatus consists of the large glass bulb *a*, of about 150 cubic centimeters capacity, and three smaller bulbs *b*, *c*, *d*, each having a capacity of about 100 cubic centimeters.

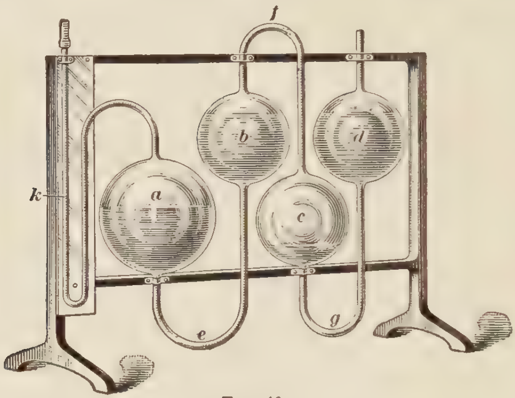

FIG. 10

They are connected by the bent tubes *e*, *f*, and *g*, and end in the bent capillary tube *k*.

The addition of these two extra globes makes it somewhat more difficult to fill this pipette. It is necessary to so arrange matters that, when the absorbing reagent fills the bulb *a*, the water shall occupy *c*, so that, when the reagent passes up into *b*, the water shall be driven into *d*. If this condition is not properly secured, as the reagent is made to pass backwards and forwards between *a* and *b*, air will either be drawn in through the water in the water seal, or else some of the water itself will be drawn over into *b*.

28. Filling the Double-Absorption Pipette.—The following is considered the best method of filling the apparatus: The empty pipette is supported in an inverted position, and an ordinary 10-cubic-centimeter pipette *p* is connected to the capillary tube *k*, as shown in Fig. 11. To the free end of the latter, a piece of narrow glass tube *t* is attached by means of a short piece of rubber tubing provided with a pinch cock *l*. Another short length of rubber tube,

also carrying a pinch cock n, is attached to m. The air within the apparatus is then swept out by passing a stream of

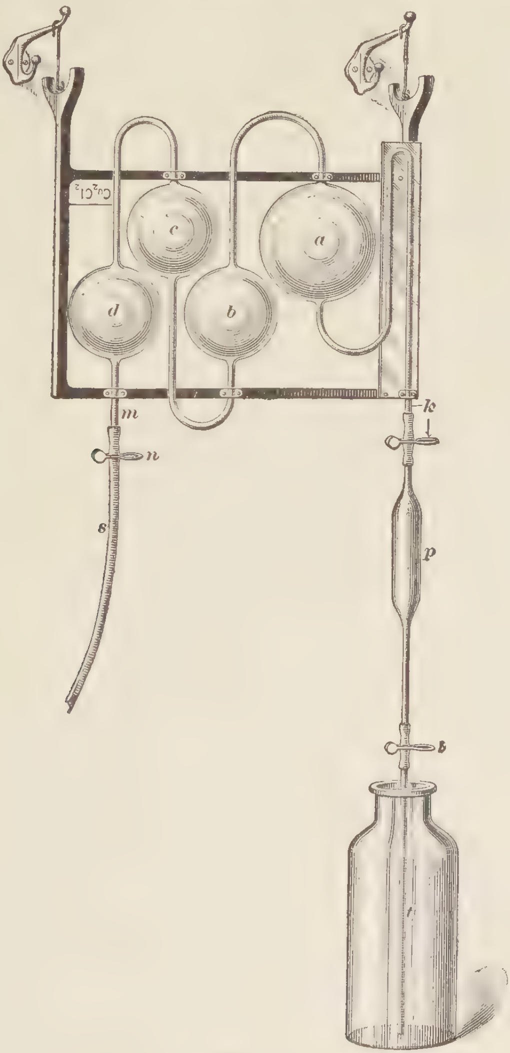

FIG. 11

some inert gas (i. e., inert toward the particular reagent that is destined to fill the pipette), such as nitrogen or carbon

dioxide, for instance. The narrow glass tube *t* is then dipped into the bottle containing the reagent in question, which is drawn up into the apparatus by applying suction through the rubber tube *s*. As soon as the globe *a* is completely filled, care being taken not to draw any liquid over into globe *b*, the clamps *n* and *l* are closed, and the tube *t* disconnected.

The apparatus is returned to its normal position, the little pipette *p* being supported by the hand. The burette, which has been previously filled with the same inert gas used for the pipette, is now attached to the rubber union at *l* by means of the bent capillary tube *t*, as shown in Fig. 12. The

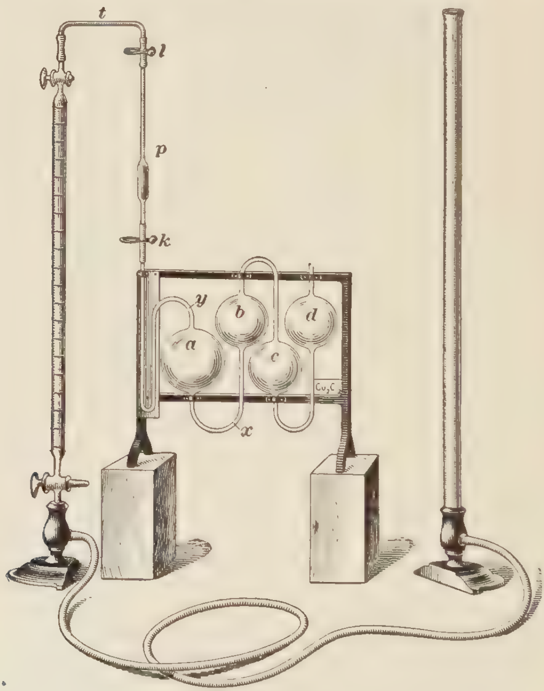

FIG. 12

reagent should now occupy the entire space between the clamp *l* and a point *x* in the bent tube, except probably for a small bubble that, most likely, will have collected at *y*. The rubber tube (see Fig. 11) is now removed, and 3 or

4 cubic centimeters of water are introduced into the globe *d* by means of a thistle funnel. This water will partly descend into the bent tube connecting *c* and *d*, and is intended to serve as a temporary water seal.

The inert gas in the burette is now slowly passed into the pipette by raising the level tube and opening the stop-cock of the measuring tube and the clamps *l* and *k*. As the gas passes in, the reagent is driven from the globe *a* to *b*, while the gas that was in *b* is expelled through the small quantity of water that was in *d*. When all the gas from the burette has been transferred to the pipette, clamp *l* is closed, and water is introduced into the globe *d* until it is nearly filled. The clamp *k* is now closed, and the little pipette *p* removed. The clamp should be opened again just to allow the liquids to sink to their natural level, and the rubber then closed by means of a plug or glass rod. The gas pipette is now properly charged, the space between the reagent and the water seal being occupied by inert gas, while the confining water occupies such a position in the globes *c* and *d* that it will neither pass over into *b* nor allow air to pass through when the reagent is being transferred backwards and forwards from *a* to *b*. The interposition of the 10-cubic-centimeter pipette in the filling operation will have secured the introduction of rather more than enough of the reagent to fill globe *a*. When, therefore, in the process of returning a gas from the absorption pipette to the burette, the reagent completely fills the bulb *a* and capillary tube, there will still remain a few cubic centimeters in globe *b*.

Since 100 cubic centimeters of gas (the capacity of the burette) may at any time be introduced into the globe *a*, it will be evident that the capacity of *b*, *c*, and *d* must not be less than this volume, otherwise they will overflow.

29. Gases Usually Estimated by Absorption.—The gases that are most frequently estimated by absorption in a simple gas pipette, and the reagents employed for this purpose are:

1. *Carbon Dioxide* CO_2.—This is absorbed by *potassium*

hydrate. Potassium hydrate of a suitable strength to serve as reagent in gas analysis is made up by dissolving 150 grams of caustic potash in 500 cubic centimeters of water. The pipette shown in Fig. 8 is used for the determination.

2. *Carbon Monoxide CO.*—The absorption agent used is *cuprous chloride.* Cuprous chloride being soluble in ammonia as well as in hydrochloric acid, either an acid or an ammoniacal solution may be used. The former is preferable, except under certain circumstances, which are described in Art. **48**, when the ammoniacal solution had to be used. The reagent is made up as follows:

(*a*) *Acid Solution.**—Thirty grams of chemically pure cuprous chloride are added to 50 cubic centimeters of water in a flask, and 150 cubic centimeters of strong hydrochloric acid are added. A few copper turnings or thin strips of copper may be placed in the brownish solution, and the flask corked up for a day or two, when the liquid will become colorless.

(*b*) *Ammoniacal Solution.*—Twenty grams of cuprous chloride are mixed with 150 cubic centimeters of water in a flask fitted with a perforated cork carrying two tubes, one reaching to the bottom, while the other ends just below the cork. The air is swept out of the flask by a stream of indifferent gas, such as hydrogen or carbon dioxide, after which the exit tube is made dip beneath the water. A stream of ammonia is then passed into the solution until the cuprous chloride has entirely dissolved; but avoid excess of ammonia. This reagent is used in the double pipette, shown in Fig. 10, and care must be taken to expose the reagent as little as possible to the atmosphere while filling the pipette (see Art. **28**).

3. *Oxygen.*—Oxygen is absorbed by *alkaline pyrogallol.* The reagent is prepared by dissolving 20 grams of pyrogallol $1:2:3 = C_6H_3(OH)_3$ in 200 cubic centimeters of a potassium-hydrate solution having the same strength as that used for the absorption of carbon dioxide.

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* If cuprous chloride is not at hand, the solution may be made by digesting copper oxide with hydrochloric acid (Sp. Gr. 1.1) in a stoppered bottle that is nearly full of copper wire. The dark solution gradually becomes lighter and when colorless is ready for use. The ammoniacal solution may be made from this by adding a slight excess of ammonia.

4. *Hydrocarbons* (*olefines*).—Hydrocarbons are absorbed by fuming *sulphuric acid* or *bromine water*. After exposure to either of these reagents, the gas is freed from either sulphur dioxide or from the vapor of bromine by being transferred to another pipette containing potassium-hydrate solution. The tubes of the pipette containing fuming sulphuric acid as reagent must be kept closed by means of a piece of glass rod and rubber tube, when the apparatus is not used.

Benzene vapor is absorbed by sulphuric acid, but not by bromine water. It is also absorbed by fuming nitric acid.

5. *Nitric Oxide*.—Nitric oxide is absorbed by *ferrous sulphate*. The ferrous sulphate is prepared by dissolving 70 grams of ferrous sulphate in 150 cubic centimeters of water. A double pipette is used for this determination. In case a double pipette is not at hand, the absorption can be made in a single pipette, but then, instead of ferrous sulphate, a solution of potassium permanganate, acidified with sulphuric acid, must be employed as absorption agent.

6. *Chlorine*, *hydrogen sulphide*, *sulphur dioxide*, *hydrochloric-acid gas*, and other acid gases are generally absorbed from gaseous mixtures by potassium hydrate.

ABSORPTION OF A GASEOUS MIXTURE

30. As a first exercise in manipulating gas apparatus, it is recommended to make an absorption of a carefully prepared mixture of gases. A mixture of carbon dioxide, oxygen, carbon monoxide, and nitrogen are especially suitable for this purpose, as these gases are constantly met with, associated together in such gaseous mixtures as furnace gases, generator gases, coal gas, water gas, etc.

The mixture is prepared by partially filling (say, about three-fourths) a collection tube similar to that shown in Fig. 7 with air. A small quantity of oxalic acid is heated with strong sulphuric acid in a test tube fitted with a cork and delivery tube, and the mixture of CO and CO_2 thus obtained is collected in the collection tube, previously mentioned, so

as to fill the remaining one-fourth. The tube now contains a mixture of the four gases, oxygen and nitrogen in the air, and CO and CO_2 collected from the decomposed oxalic acid. It will be obvious that the order in which the gases are to be absorbed from a mixture deserves careful consideration, as, for instance, in this case, the oxygen must be absorbed before the carbon monoxide, otherwise the reagent used to absorb the latter gas (cuprous chloride) would be acted on by the oxygen present.

The different gases should be estimated in the following order:

Carbon dioxide, absorbed by means of potassium hydrate.
Oxygen, absorbed by means of pyrogallol.
Carbon monoxide, absorbed by means of cuprous chloride.
Nitrogen, estimated by difference.

31. Preparation of Water Used in Gas Burette. The water that is used in the gas burette has to be saturated with the gaseous mixture to be analyzed before beginning the analysis, in order to prevent absorption of the mixture during the analysis, and thus obviating the exactness of the result. For this purpose, a stoppered bottle holding about 300 or 350 cubic centimeters is filled with distilled water and inverted in a water trough. About 100 cubic centimeters of the gaseous mixture is bubbled up into the bottle, which is then closed with the stopper, and the gas thoroughly shaken with the remaining water for a few minutes.

Some of this saturated water is poured into the level tube of the gas burette, and the stop-cock at the foot of the measuring tube is turned so as to establish communication between the two tubes. It should be remarked here that this stop-cock must not be touched again through the entire process of the analysis, the passage of the gas to and from the measuring tube and the various pipettes used being entirely controlled by the upper stop-cock of the measuring tube. The bent capillary connecting tube is then attached to the top of the measuring tube, and the latter is completely filled with water by raising the level tube and opening the

stop-cock at the top of the measuring tube, until the liquid drops from the end of the capillary tube. The rubber connection on the collecting tube containing the gas is filled up with a drop of water and joined to the end of the bent capillary (see Fig. 7) and the connections secured with thin binding wire. The level tube is lowered and the pinch cock on the collecting tube and the upper stop-cock of the measuring tube are opened, whereby gas is drawn over into the latter tube. When sufficient gas has thus been transferred, the pinch cock and stop-cock are closed, and the two tubes disconnected. One minute is allowed to elapse for the water to drain down the walls of the measuring tube, when the volume of the gas introduced is read off by lowering the level tube until the level of the water in it and in the measuring tube is the same. The graduation mark that coincides with the bottom of the meniscus represents the volume of gas taken for the analysis.

32. It is convenient to employ, when possible, exactly 100 cubic centimeters of the gas under analysis, in which case the number of cubic centimeters of the various constituents that are absorbed represents the percentage of each ingredient in the gas mixture. If, therefore, more than 100 cubic centimeters have first been introduced into the apparatus, the excess may be removed by raising the level tube until the gas is compressed to exactly 100 cubic centimeters, then, keeping the water in that position by pressing a finger upon the rubber tube, the stop-cock at the top is momentarily opened. This allows the excess of gas to escape, leaving exactly 100 cubic centimeters at atmospheric pressure. This is controlled by again lowering the level tube until the water in each tube is at the same level, when the gas should be found to occupy 100 cubic centimeters.

33. Determination of Carbon Dioxide.—We are now ready to begin the first determination, that is, that of carbon dioxide, and, for this purpose, the burette is attached to the absorption pipette, containing potassium hydrate, in the

manner shown in Fig. 13. Before the two pieces of apparatus are, however, joined, the potassium hydrate solution is drawn up so as to completely fill the globe *a*, and the bent capillary tube to the mark *c*, which is made on the white plate behind it. The pinch cock keeps it in this position. After the rubber connections have been secured with

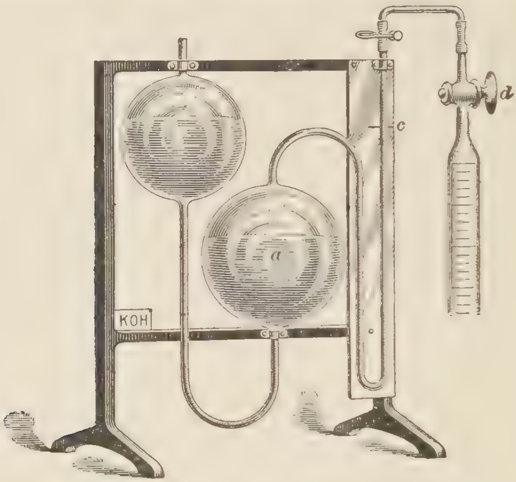


FIG. 13

binding wire, the pinch cock is opened, when, if the joints are tight, the reagent will not sink from its position at *c*. The pinch cock may be kept open by lifting it so that it nips the glass tube. The level tube is now raised (being handled exclusively by its foot) and the stop-cock *d* at the top of the measuring tube is opened.

The gas is thus transferred completely to the bulb *a* of the pipette; 2 or 3 drops of water from the measuring tube are allowed to follow the gas into the bulb (by doing so, the capillary tube of the pipette is washed each time the apparatus is used), after which the stop-cock *d* is closed. The gas is allowed to remain in contact with the potassium-hydrate solution for about 5 minutes, during which time the apparatus is gently shaken so as to moisten the sides of the globe with the reagent. The level tube is again lowered and the stop-cock *d* opened, and thus the gas returned to the measuring

tube. As soon as the potassium-hydrate solution reaches the point in the capillary tube opposite *c*, the stop-cock is closed.

The utmost care should be exercised not to allow the reagent to come in contact with the rubber connections, or to pass into the measuring tube. The pressure tube is then held in such a position that the water stands at an equal level in both tubes, and, after waiting 1 minute for the water to drain down the walls of the tube, the volume that the gas now occupies is read off.

The operation of filling the pipette with the gas is once repeated in exactly the same way as previously described, in order to be sure that all the carbon dioxide has really been absorbed by the reagent, and the volume is again read off at atmospheric pressure. If the two readings agree, the first absorption was complete. For example,

Original volume of gas	= 1 0 0 c.c.	
Volume after absorption by KOH	= 8 8 c.c.	
Carbon dioxide	= 1 2 c.c.	= 12%

34. Determination of Oxygen.—The potassium-hydrate pipette is now detached from the bent capillary tube at the joint immediately above the pinch cock Fig. 13, and replaced by the double pipette containing the alkaline solution of pyrogallol. Before the latter is connected, the reagent is drawn up into the capillary tube to a marked point, which is, as nearly as possible, the same distance from the pinch cock as that on the pipette used for the previous determination. The gas is transferred for absorption exactly as in the former case, and is left in contact with the reagent, with occasional gentle shaking, for 10 minutes. It is then returned to the measuring tube, the same care being taken to bring the reagent exactly to the mark on the capillary tube. The stop-cock is closed, and, after allowing time for the water to drain off the walls of the measuring tube, the volume of the residual gas is read off at atmospheric pressure. For example,

Volume of gas before absorption of oxygen	= 8 8 c. c.	
Volume of gas after absorption of oxygen	= 7 3 c. c.	
Oxygen	= 1 5 c. c.	= 15%

35. Determination of Carbon Monoxide.—After finishing the determination of oxygen as described above, the double pipette containing the pyrogallol is disconnected, and replaced by one containing cuprous chloride in acid solution, the reagent being previously drawn over into the capillary tube to a mark in the same relative position as in the two previous cases. The gas is transferred to the pipette and allowed to remain exposed to the reagent; after the lapse of 10 minutes, it is retransferred to the measuring tube of the burette, and its volume determined as previously stated. For example,

Volume of gas before absorption of carbon monoxide	= 73 c. c.	
Volume of gas after absorption of carbon monoxide	= 60.5 c. c.	
Carbon monoxide	= 12.5 c. c.	= 12.5%
Volume of residual gas (nitrogen)	= 60.5 c. c.	= 60.5%

Hence, the composition of the gas under examination is:

Carbon dioxide	= 12
Carbon monoxide	= 12.5
Oxygen	= 15
Nitrogen (by difference)	= 60.5
Total	= 100.0

A duplicate analysis was made, and the correctness confirmed.

ESTIMATION OF GASES BY COMBUSTION

DETERMINATION OF HYDROGEN

36. When hydrogen and oxygen combine according to the equation

$$2H_2 + O_2 = 2H_2O$$

the 2 volumes of hydrogen and 1 volume of oxygen practically cease to occupy space, since the volume of the condensed water is inappreciable. By measuring the contraction

of volume that takes place under these circumstances, and multiplying this by $\frac{2}{3}$, the volume of hydrogen that was burnt is determined.

The estimation of hydrogen is then accomplished by mixing a measured volume of the gas with a measured volume of air—rather greater than the volume estimated to be required to furnish the necessary volume of oxygen—and by causing the mixture of hydrogen and oxygen to unite by one of the methods described below. After the combination has been accomplished, the residual gas is again measured, and two-thirds of the contraction will represent the volume of the hydrogen consumed.

Two methods that are mostly used in practical analytical work are given below.

37. Combustion of Hydrogen by Means of Palladiumized Asbestos.—The hydrogen is mixed with an excess of the required volume of air in a gas burette that is attached to a single-absorption pipette charged with distilled water. The capillary tube that forms the connection between the absorption pipette and the measuring tube contains a thread of asbestos upon which has been deposited a quantity of finely divided palladium. As the gas is passed from the measuring tube of the burette to the pipette, it comes in full contact with the palladiumized asbestos (which is gently warmed by means of a small flame), and the hydrogen and oxygen are thereby caused to unite. The gas is finally returned to the burette and measured.

38. Preparation of Palladiumized Asbestos.—The capillary tube containing the palladiumized asbestos is prepared in the following manner: .25 gram of palladium foil is dissolved in as little aqua regia as possible in a small porcelain dish and the solution evaporated to dryness on the water bath. The residue is moistened with 3 or 4 drops of strong hydrochloric acid, and 1 cubic centimeter of water added. The mixture may be gently warmed to complete the solution. To this red-brown solution, when cold, 20 drops

of a cold saturated solution of sodium formate are added. Into this mixture, which will not exceed 2.5 cubic centimeters in volume, .25 gram of asbestos thread is immersed, which will soak up the whole of the liquid. It is self-evident that the thread must be sufficiently fine to admit of being pushed into a capillary tube of 1 millimeter bore. It may be obtained by unraveling a piece of asbestos cloth so as to get single strands. It is cleaned from grease by treating it once or twice with a little carbon disulphide in a test tube and then spreading it out on a clean piece of paper to dry, after which it should be heated for a few minutes on a piece of platinum foil. A quarter of a gram will be about 60 centimeters in length.

A strong solution of sodium carbonate is added by means of a dropper and gently worked into the soaked thread with a glass rod, until the mixture is alkaline, and the dish placed on a water bath. A gentle heat is sufficient to reduce the palladium, which is then precipitated throughout the asbestos as a black deposit. When the contents of the dish are dry, they are rinsed 3 or 4 times with hot water, in order to dissolve out any soluble salts. The thread is then removed and cut into short pieces, each about 4 centimeters long. One of these pieces is straightened out by a gentle twisting of the fingers, and laid on a piece of blotting paper for a few minutes, to remove any superfluous water. It is then introduced into a thick-walled capillary tube, 1 millimeter bore and about 15 centimeters long. When the thread has been pushed a little way into the tube, it may readily be drawn into the middle by applying a gentle suction to the other end. The thread is then dried by gently warming the tube and slowly drawing air through it, after which the tube is bent at right angles, about 3 centimeters from each end. The same piece of palladiumized asbestos may be used for several combustions.

39. Analysis of a Gaseous Mixture of Hydrogen and Air.—As an exercise of this analysis, a mixture of hydrogen and air may be conveniently employed. About

20 cubic centimeters of pure hydrogen are introduced into the gas burette, and the volume accurately measured. The level tube is then lowered, and a quantity of air introduced into the burette until the total volume amounts to between 80 and 85 cubic centimeters; or, in other words, about 60 to 65 cubic centimeters of air are added, and the volume is again accurately measured.

The gas burette is now attached to a single gas pipette charged with water by means of the capillary combustion tube containing the palladiumized asbestos prepared according to Art. **38,** instead of the usual connecting tube. The palladium is gently heated by moving a Bunsen flame along the tube, which must be kept warm through the entire operation, so as to prevent water, the product of the combustion of hydrogen and oxygen, from condensing in it. The temperature of the tube, however, must not approach a visible redness. The gas is allowed to pass slowly over the warm palladium, which will be seen to glow at the end toward the incoming gas. When the entire volume of the gas has been passed over into the pipette, it is slowly drawn back again into the burette. This process is repeated once or twice, although, if the palladiumized asbestos is in good order, one repetition is usually sufficient, after which the residual gas is measured. It is then passed once more into the pipette, and back, and measured again. If the two measurements agree, the process is complete. For example,

Original volume of hydrogen taken	=	20.5 c. c.
Excess of air	=	63.3 c. c.
Total volume of mixture	=	83.8 c. c.
Volume of combustion	=	53.2 c. c.
Contraction	=	30.6 c. c.

$30.6 \times \frac{2}{3} = 20.4$ c. c. = volume of hydrogen found

40. For the analysis of marsh gas and similar hydrocarbons, some chemists prefer the apparatus shown in Fig. 14, and which is based on the occlusion of hydrogen by palladium black. The gas burette *A* and the absorption pipette *B*

are joined together by means of the capillary tubes *e*, *e* and the tube *h*. This tube *h* is about 4 millimeters internal

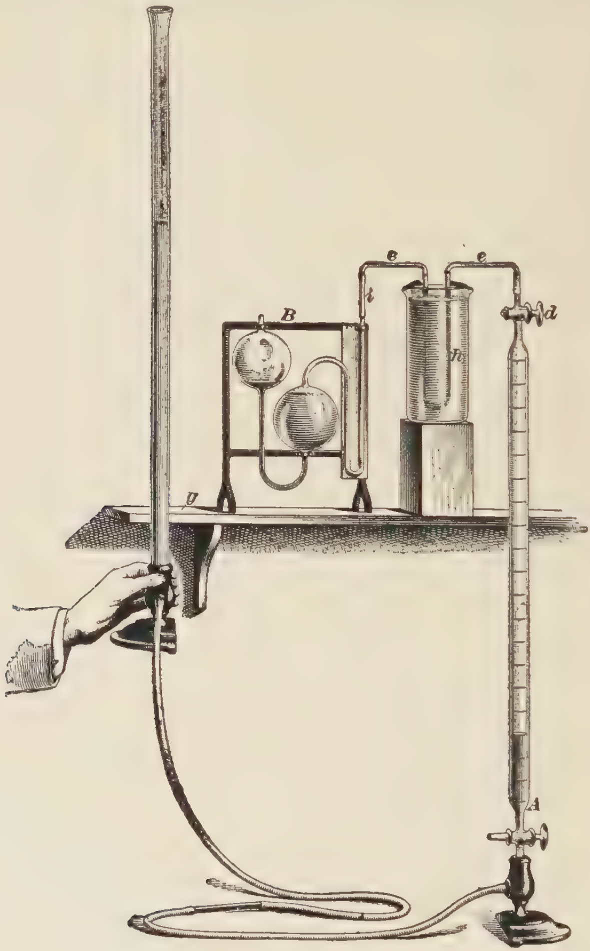


Fig. 14

diameter and 20 centimeters total length, and it contains 4 grams of palladium sponge.

The gas pipette on the stand *g* is filled with water, and its only use, as in the previous arrangement, is to render it possible to repeatedly pass the gas through the tube containing

the palladium. To determine the amount of hydrogen in a gaseous mixture, the gas is measured in the burette joined to the pipette *B*, which is filled with water nearly to *i*. The tube *h* is placed in a good-sized beaker containing water of from 90° to 100°, and, after opening the stop-cock *d*, the gas is driven 3 or 4 times back and forth through the palladium by raising and lowering the level tube.

The hot water is then replaced by water of the temperature of the room, and the gas is again passed twice through the **U** tube, in order to cool it completely. On drawing the gas so far back into the measuring tube that the water in the pipette again stands near *i*, the gas is measured, and the difference between the two measurements, made before and after the absorption, corresponds to the hydrogen plus the amount of air enclosed in the **U** tube when the apparatus was put together. This air volume, with its oxygen contents, may be determined with sufficient exactness once for all by closing, with a piece of rubber tube and glass rod, one side of the tube filled with palladium, cooling the tube to about 9° by placing it in cold water, and then, after connecting it by a capillary with a gas burette completely filled with water, warming it to 100° by placing it in boiling water. The expansion of the enclosed air volume corresponds to a difference of temperature of 91°, i. e., to a third of the enclosed volume of gas.

The palladium is regenerated after the reaction by first leading air over it, whereby it becomes quite hot, removing any drops of moisture that may collect, so that the palladium may easily be shaken out in the form of a dry powder, and then superficially oxidizing the metal by heating it on the lid of a platinum crucible.

41. Combustion of Hydrogen by Explosion With Air.—For this purpose, the mixture of hydrogen with excess of air is transferred to a special piece of apparatus known as an *explosion pipette*, in which are sealed two pieces of platinum wire, whereby the gaseous mixture may be ignited by a spark from a Ruhmkorff coil. One form of these explosion pipettes, in which the gas is confined over water, is shown in

Fig. 15. Water that has been acidulated with sulphuric acid and boiled to expel any dissolved gases is introduced at *a* until the bulb *b* is just full, and the liquid stands level in the other limb. On the tubes *a* and *c*, pieces of thick-walled rubber tubes are securely wired, and a pinch cock is placed on each. At *d*, two platinum wires are sealed into the glass, between which the electric spark is passed when the gas is to be exploded. In the lower part of the tube at *c*, two platinum electrodes are fused into the glass. These are for the purpose of adding a small quantity of electrolytic gas to the mixture, when the proportion of combustible gas is so small that no explosion will take place when the electric spark is passed.

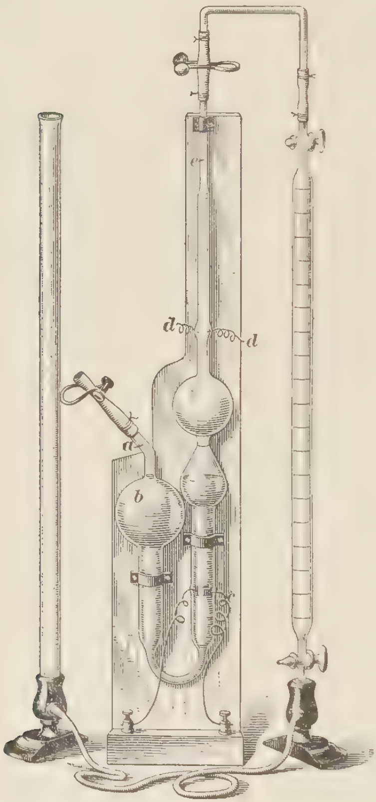


Fig. 15

Before the electrolytic gas is generated, the mixture under analysis is transferred to the measuring tube, which is then detached from the explosion pipette. The two wires from a battery, not from the coil, are then connected to the electrodes *c* and the oxygen and hydrogen that is evolved is allowed to escape. The current is allowed to pass for about 15 minutes, in order to saturate the water, after which the current is stopped and the liquid driven up to the usual mark on the capillary. The burette is reconnected and the gas returned to the pipette. A small quantity of electrolytic gas is then generated, and thoroughly

mixed with the gas already present before exploding. It is not necessary to know the volume of the gas thus added, as it entirely disappears when fired.

42. As a first exercise in the use of an explosion pipette, a mixture of pure hydrogen and air may be advantageously employed. About 10 to 15 cubic centimeters of hydrogen are introduced into the gas burette, and, after being exactly measured, about 60 to 70 cubic centimeters of air are added, and the mixed gases again measured. The burette is then attached to the explosion pipette, the liquid in the latter being previously drawn up to a mark on the capillary tube *c*. The gas is then passed over into the pipette, and the clamps on the rubber tubes are both closed. The wires from the induction coil are attached to the wires at *d*, and the electric spark allowed to pass. The explosion, although not at all violent, will cause a momentary expansion within the apparatus, but, if sufficient liquid is present, no gas will be driven out of the bulb tube. The thick rubber tube on *a* being closed, the small quantity of air that is in the bulb *b* serves as a cushion, so to speak, at the moment of the explosion, and thus relieves the other part of the apparatus from undue pressure. The moment after passing the spark, the tube *a* is opened, and then the gas is returned to the burette and measured. The contraction represents the hydrogen and atmospheric oxygen with which it has combined to form water, and two-thirds of this shrinkage is the volume of hydrogen that was present. For example,

Volume of hydrogen taken	= 12.5 c. c.
Volume of air	= 63.3 c. c.
Volume of hydrogen and air	= 75.8 c. c.
Volume after explosion	= 57.5 c. c.
Contraction	= 18.3 c. c.

$18.3 \times \frac{2}{3} = 12.2$ c. c. = volume of hydrogen found

43. For practice in the use of electrolytic gas, the following experiment is recommended: A quantity of air, say 55 or 60 cubic centimeters, is introduced into the burette, and its volume measured in the usual way. The current from

four or five Grove's cells, or its equivalent from any other source, is passed through the dilute acid in the explosion pipette by means of the electrodes at *c*, Fig. 15, for about 10 minutes, and the liquid shaken up once or twice with the gas in order that it may become saturated. The current is then turned off and the liquid drawn up to the mark on the capillary. The burette containing the measured volume of air is attached in the usual manner. About 12 cubic centimeters of electrolytic gas are then generated in the pipette and drawn over into the burette. The actual amount of electrolytic gas that has been added may be ascertained by measuring the total volume of gas in the burette. It is not necessary, however, to know this volume exactly, and a very little practice will enable the student to estimate the volume by the space it occupies in the explosion pipette as it is generated. The mixture of air and electrolytic gas is then passed twice backwards and forwards from the burette, to insure a complete mixing, after which the clamps are closed and the mixture exploded. The residual gas is transferred back to the burette and measured, when the volume should be exactly the same as previously introduced.

Usually, after the first experiment, the volume of the residual air is not exactly identical with that originally taken, owing to the imperfect saturation of the liquid with the various gases. If this is the case, a similar quantity of electrolytic gas should again be added, and the mixture exploded once more after thorough admixture. The volume of the residual gas after this second explosion should then exactly agree with that which was measured after the first operation. The process may be repeated with varying amounts of electrolytic gas, and the volume of the residue will be found to remain constant.

DETERMINATION OF MARSH GAS

44. Explosion of Marsh Gas Over Water.—The product of an explosion of marsh gas (methane) and air is carbon dioxide and water, as is seen from the subjoined equation:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

The equation shows that if methane is exploded with air, the volume of CO_2 obtained is equal to the original volume of marsh gas present, and also that 3 volumes present before the explosion are reduced to 1 volume, that of CO_2, after the explosion. The contraction, therefore, is two-thirds of the original volume of the reacting gases; or, in other words, the contraction is equal to twice the carbon dioxide produced, or to twice the volume of marsh gas exploded.

Owing to the effect of pressure in increasing the solubility of carbon dioxide in water, it is only possible to obtain accurate results when mercury is used as the confining liquid.

45. Determination of Loss of Carbon Dioxide by Solution.—With a view to ascertaining the extent of the loss of carbon dioxide by solution in water, when the explosion is performed over that confining medium, the following experiments were made with the apparatus shown in Fig. 15:

1. 67 cubic centimeters of a mixture of air and carbon dioxide, containing 9 per cent. CO_2, were introduced into the apparatus and 12 cubic centimeters of electrolytic gas added. After explosion, the remaining volume occupied 66.7 cubic centimeters.

$$\text{Loss of } CO_2 = .3 \text{ c. c.} = .4\%$$

2. 78 cubic centimeters of a similar mixture, containing 20 per cent. CO_2; 15 cubic centimeters electrolytic gas added. Volume after explosion = 77.2 cubic centimeters.

$$\text{Loss of } CO_2 = .8 \text{ c. c.} = 1\%$$

3. 50.8 cubic centimeters of a similar mixture, containing 40 per cent. CO_2; 15 cubic centimeters electrolytic gas added. Volume after explosion = 49 cubic centimeters.

$$\text{Loss of } CO_2 = 1.8 \text{ c. c.} = 3.5+\%$$

About the same volume of electrolytic gas was added 3 times, and the mixture exploded and measured after each addition; the volumes obtained were 47.4 cubic centimeters, 46.2 cubic centimeters, and 45.2 cubic centimeters, showing a fairly regular loss of carbon dioxide.

4. 47.2 cubic centimeters of air containing 36.4 per cent. of CO_2.

(*a*) 20 c. c. electrolytic gas added; after explosion volume = 45.6 c. c.
(*b*) 12 c. c. electrolytic gas added; after explosion volume = 45.0 c. c.
(*c*) 20 c. c. electrolytic gas added; after explosion volume = 43.6 c. c.

(*a*) loss = 1.6 c. c., or 3.4%
(*b*) loss = 0.6 c. c.
(*c*) loss = 1.4 c. c.

Experiments 1, 2, and 3 show that with about the same force of explosion, the loss of CO_2 increases as the percentage rises, while experiment 4 shows that with the same percentage of carbon dioxide, the amount absorbed depends on the force of the explosion.

46. Explosion of Marsh Gas Over Mercury.—An explosion pipette in which mercury is employed is shown in Fig. 16. It differs from the ordinary absorption pipette only in containing two platinum wires fused in the upper part of bulb *a*, and being furnished with a stop-cock *c*, in order to close the communication between the two bulbs. Before the apparatus is connected to the burette containing the measured mixture for explosion, the mercury is driven over into the capillary tube to a fixed mark by blowing through the rubber tube on the upper bulb *b*, and, similarly, when the gas is transferred from the burette to the explosion

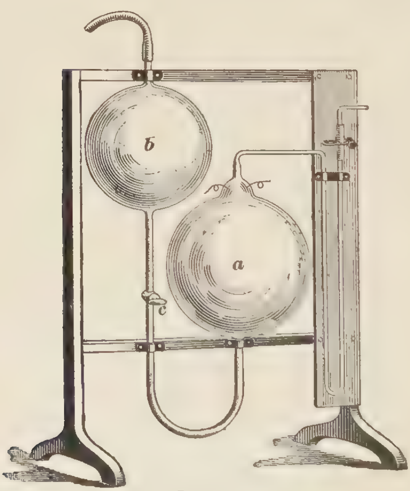


FIG. 16

pipette, it must be drawn over by applying suction to the same rubber tube. The water from the burette should be made follow the gas so as to just fill the capillary tube, but without being allowed to enter the bulb. Before exploding the mixture, both the pinch cock and stop-cock are closed. After the explosion, the gas is transferred to the burette and measured. The explosion pipette is then disconnected and replaced by the simple-absorption pipette containing potassium hydrate, and the carbon dioxide is absorbed in the usual way.

47. Analysis of Mixtures of Hydrogen, Methane, and Nitrogen.—Many gaseous mixtures that constantly come under analysis (such as coal gas, producer gas, water gas, blast-furnace gases, etc.), contain varying quantities of these three gases along with others. After all the other gases have been estimated by absorption in their respective reagents, the hydrogen and marsh gas in the residue are determined by one of the following methods, while the nitrogen is estimated by difference:

48. *First Method.*—The gas is mixed with an excess of air, and the hydrogen estimated by combustion, by means of palladiumized asbestos, as described in Art. **37.** Under these conditions the marsh gas does not burn. The marsh gas is then determined by exploding the residual mixture and absorbing the carbon dioxide produced, as previously described. The volume of nitrogen is found by deducting from the original volume of gas the hydrogen and marsh gas thus determined.

A description of an analysis performed by the writer will make the proceedings clear to the student.

To the action of the following reagents, 100 cubic centimeters of coal gas were exposed:

(*a*) Potassium hydrate, to absorb carbon dioxide.

(*b*) Alkaline pyrogallol, to absorb oxygen.

(*c*) Fuming sulphuric acid, to absorb olefines and benzene vapor.

(*d*) Ammoniacal cuprous chloride, to absorb carbon monoxide.*

The residual gas, measuring 86.6 cubic centimeters, was returned to the cuprous-chloride pipette, while the burette was disconnected and the water in it (previously saturated with coal gas) was replaced by water saturated with air. Then, 20 cubic centimeters of the gas were transferred to the burette (the rest being reserved for a subsequent experiment), and air was added in more than sufficient quantity for the complete combustion of the hydrogen.

Volume of gas = 20.0 c. c.
Volume of gas + air = 64.4 c. c.

This mixture was then passed over the palladiumized asbestos.

Volume after combustion of hydrogen = 48.2 c. c.
Therefore, $64.4 - 48.2 = 16.2$ c. c. = contraction,
and $16.2 \times \frac{2}{3} = 10.8$ = volume of hydrogen present in 20 c. c. of gas.

To the residual gas (consisting of marsh gas, nitrogen, and a small surplus of oxygen) an excess of oxygen was added.

Volume of residual gas = 48.2 c. c.
Volume of residual gas + air = 69.6 c. c.

The mixture was then exploded, and the carbon dioxide absorbed.

Volume after explosion = 52.8 c. c.

Therefore, $69.6 - 52.8 = 16.8$ = contraction.

Volume after absorption of CO_2 = 44.4 c. c.

Therefore, $52.8 - 44.4 = 8.4$ = volume of CO_2 produced.
Therefore,

8.4 c. c. = volume of marsh gas present in 20 c. c. of gas.

20.0 c. c. − (10.8 + 8.4) = .8 c. c.
= volume of nitrogen in 20 c. c. of gas.

* When the absorption of carbon monoxide is to be followed by the combustion of hydrogen with palladiumized asbestos, the ammoniacal solution of cuprous chloride should be used.

Since the original volume of gas taken for analysis was 100 cubic centimeters,

then $$\frac{10.8 \times 86.6}{20} = 46.76\% \text{ of hydrogen,}$$

and $$\frac{8.4 \times 86.6}{20} = 36.37\% \text{ of marsh gas,}$$

and $$\frac{.8 \times 86.6}{20} = 3.46\% \text{ of nitrogen}$$

49. *Second Method.*—By this method, to the mixture of hydrogen and marsh gas and nitrogen sufficient air or oxygen is added for the complete combustion of both combustible gases, and the mixture exploded. The contraction is then measured, after which the carbon dioxide is absorbed and the volume again measured. From these data, the volumes of the hydrogen and marsh gas can be calculated. As already explained in Art. **44,** the contraction due to the combustion of marsh gas is twice the volume of carbon dioxide; if, therefore, the volume of carbon dioxide is ascertained (by absorption with potassium hydrate), and twice this volume be deducted from the contraction on explosion, the product will represent the contraction due to the combustion of the hydrogen.

Let C = contraction on explosion;

C' = volume of CO_2 produced (i. e., contraction on absorption with KOH).

Then, $C - 2C'$ = contraction due to the hydrogen,

and $\frac{2}{3}(C - 2C')$ = volume of hydrogen.

Again, since the volume of carbon dioxide produced is the same as the volume of marsh gas burned,

$$C' = \text{volume of marsh gas}$$

The following will make this perfectly clear: A portion of the mixture of hydrogen, marsh gas, and nitrogen employed in the previous example (being the residual gas after the removal of the absorbable constituents from a sample of

coal gas) was measured in the burette, and an excess of air added.

$$
\begin{aligned}
&\text{Volume of gas taken} &&= 14.2 \text{ c. c.}\\
&\text{Volume of gas} + \text{air} &&= 97.6 \text{ c. c.}\\
&\text{Volume after explosion} &&= 74.2 \text{ c. c.}\\
\text{Therefore, contraction } C = 97.6 - 74.2 &&&= 23.4 \text{ c. c.}\\
\text{After absorption by } KOH, \quad \text{volume} &&&= 68.2 \text{ c. c.}\\
\text{Therefore, } \quad C' = 74.2 - 68.2 &&&= 6.0 \text{ c. c.}
\end{aligned}
$$

Hence, volume of H in 14.2 c. c. of the gas

$$= \tfrac{2}{3}(23.4 - 12) = 7.6 \text{ c.c.},$$

and volume of CH_4 in 14.2 c. c. of the gas $= 6.0$ c.c.,

and volume of N in 14.2 c. c. of the gas

$$= 14.2 - (7.6 + 6.0) = 0.6 \text{ c. c.}$$

Calculating the percentage as in the previous instance,

$$\frac{7.6 \times 86.6}{14.2} = 46.3\% \text{ of hydrogen}$$

6

$$\frac{6 \times 86.6}{14.2} = 36.\cancel{5}\% \text{ of marsh gas}$$

7

$$\frac{.6 \times 86.6}{14.2} = 3.\cancel{6}\% \text{ of nitrogen}$$

In cases where the gas under analysis contains a relatively large proportion of nitrogen, as, for example, in the case of producer gas or blast-furnace gases, the addition of air would dilute the gas to such an extent as to render it non-combustible. Under these circumstances, therefore, either oxygen must be substituted for air, or else, after sufficient air has been added to furnish the requisite amount of oxygen, a few cubic centimeters of electrolytic gas may be added to the mixture. The electrolytic gas for this purpose may be generated in the pipette described in Art. **41**, and then transferred to the mercury-explosion pipette.

THE NITROMETER AND GASVOLUMETER

50. The **nitrometer** and the **gasvolumeter,** which were invented by Lunge, simplify gas analyses very much, and may be used for many determinations where gases are evolved. They are made in several forms; but only those forms that have given the best satisfaction are described.

The form of gasvolumeter described was designed by Jopp.

The nitrometer, Fig. 17 (*a*), consists of two glass tubes *e*, *f*, connected by a rubber tube. The tube *e* is provided with a three-way stop-cock *l*, which can be closed, can make connection between *e* and the funnel *g*, or between *e* and the capillary tube *h*. The tube *e* may or may not be graduated; when used in connection with a gasvolumeter, graduation is unnecessary.

The gasvolumeter, Fig. 17 (*b*), consists of three tubes *a*, *b*, and *c*, connected by rubber tubes and the T tube *d*. The tubes *a*, *b* are graduated, and *a* is provided with a three-way stop-cock opening into the capillary tubes *i* and *j*; *b* is provided with a stop-cock *k*, which, if the apparatus is to be adjusted only once, may be omitted, having the end of *b* simply drawn to a point, which may be closed by fusion. To adjust the apparatus, the thermometer and barometer are read.

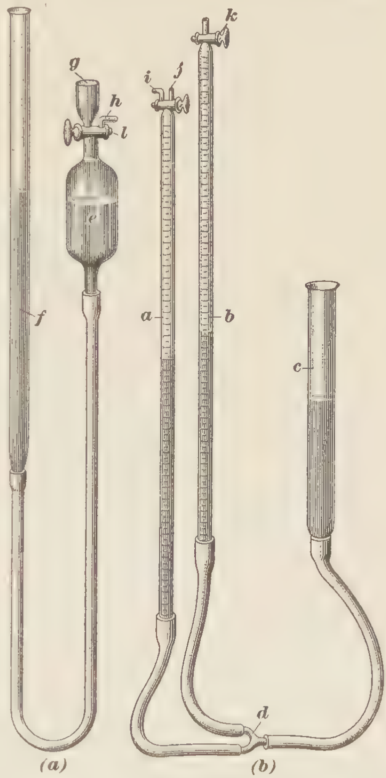


FIG. 17

The volume that 25 cubic centimeters of standard dry air (at 760 millimeters pressure and 0° C.) will occupy if measured moist at the observed temperature and pressure is calculated, and this calculated volume of air is admitted to the tube *b* at atmospheric pressure and temperature, and the cock *k* closed. The liquid in the tubes *a*, *b*, and *c* is mercury; and since the three tubes are connected, if any volume

of gas is confined in *a* and the pressure tube *c* adjusted so that the mercury in *b* stands at the 25-cubic-centimeter mark, and that in *a* is at the same level, the gas in *a* will be compressed until it occupies the volume it would occupy if dry and at normal pressure and temperature. It is apparent that if this instrument is substituted for the gas burette and readings made when the mercury in *b* stands at the 25-cubic-centimeter mark and in *a* at the same level, the volumes read in *a* are the volumes the gases would occupy under normal conditions. In this way the rather tedious calculations are avoided.

In making analyses of solid or liquid substances by measuring a gas evolved, it is not alone necessary to know the space that the evolved gas will occupy under normal conditions, but it is also necessary to know how much this gas will weigh. This weight may be calculated by multiplying the number of cubic centimeters by the weight of 1 cubic centimeter; but this calculation may be saved by the gasvolumeter. Take, for example, the gas NO. Twenty-five cubic centimeters of dry NO under normal conditions weigh 33.6 milligrams. If we have NO in the tube *a* and set the pressure tube *c* so that the mercury in *b* stands at 33.6 and in *a* at the same level, we can read from *a* the number of milligrams of NO. Obviously similar calculations can be made for any other gases and points can be found on tube *b* at which the mercury can be set to read milligrams of any gas in tube *a*.

In making a gas analysis with this apparatus, the gas is measured in tube *a*, adjusting the pressure so that the mercury in *b* stands at the 25 mark and in *a* at the same level. Then turn the stop-cock *l* of the nitrometer, Fig. 17 (*a*), so as to open *h* and by raising *f* fill *e* with mercury, close the cock and connect *h* and *i*. Lower the tube *f* and raise tube *c*. Now, by opening the cocks, the gas can be transferred to *e*. Close the cocks and disconnect *h* and *i*. Pour the absorbing reagent into funnel *g* and by carefully turning the cock *l* and regulating with the tube *f*, introduce the reagent into *e*. Care must be

taken to lose no gas and introduce no air here. Close the cock *l* and shake *e* until the absorption is complete. Return the gas to *a* and measure. Nitrates and nitrites are decomposed by large excess of sulphuric acid and mercury according to the equations:

$$2NaNO_3+3Hg+4H_2SO_4 = 3HgSO_4+Na_2SO_4+4H_2O+2NO$$

$$2NaNO_2+Hg+2H_2SO_4 = HgSO_4+Na_2SO_4+2H_2O+2NO$$

The nitrogen in these compounds can therefore be readily determined with the nitrometer. About .2 gram of nitrate dissolved in 2 cubic centimeters of water is carefully introduced through *g* into *e*, Fig. 17 (*a*). Wash the funnel *g* with 1 cubic centimeter of water, but be careful to admit no air into *e*. Then carefully introduce 5 cubic centimeters of strong sulphuric acid through *g* into *e*, then two lots of 3 cubic centimeters each to rinse thoroughly the funnel *g*. The mixing is effected by tipping the tube *e* and raising and lowering *f*. When the reaction is complete and the apparatus has cooled off, transfer the NO to tube *a* and measure, adjusting the mercury in *b* so that it stands at 33.6, and that in *a* at the same level. The number of milligrams of NO can then be read from tube *a*.

Determinations may sometimes be made by generating gas in an outside vessel, such as a flask, and collecting the gas evolved in *a* or *e* and afterwards transferring to *a*.

The direct estimation of carbonates by evolution of carbon dioxide may be made. The amount of manganese dioxide may be determined by measuring the carbon dioxide evolved by the action of manganese dioxide on oxalic acid in the presence of sulphuric acid, according to the equation:

$$MnO_2+H_2SO_4+H_2C_2O_4 = MnSO_4+2H_2O+2CO_2$$

The available oxygen in manganese dioxide, potassium permanganate, and bleaching powder may be estimated by

measuring the oxygen evolved by the action of hydrogen peroxide according to the equations:

$$MnO_2 + H_2SO_4 + H_2O_2 = MnSO_4 + 2H_2O + O_2$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

$$CaCl(OCl) + H_2O_2 + H_2O = CaCl_2 + 2H_2O + O_2$$

In performing these determinations, the weighed solids are introduced into the flask with water; in the case of manganese dioxide and potassium permanganate dilute sulphuric acid is added. The reagent, which in the three cases mentioned is hydrogen peroxide, is placed in a test tube in the flask. The flask is closed with a stopper carrying a tube and is connected with *h* or *i*. The stop-cock is then turned so as to connect *e* with *g* or *a* with *j*, and the level tube raised so as to fill *e* or *a* with mercury. Then the cock is turned so as to connect *e* or *a* with the flask and the level tube slightly lowered. The flask is tipped so as to empty the contents of the test tube into the liquid in the flask. During the evolution of the gas the level tube is lowered somewhat so as not to have excessive pressure in the apparatus. When all the gas has been evolved, the level tube is raised until the gas in *e* or *a* is under atmospheric pressure, the apparatus is allowed to assume its original temperature, the cock is closed, and the gas measured.

ANALYSIS OF CHIMNEY GASES

51. The analysis of chimney gases is a frequent occurrence in factories and works of all kinds, the percentage (by volume) of oxygen, carbon dioxide, carbon monoxide, and nitrogen being, as a rule, required. The determination of these gases has been already described in the preceding articles, but as especially constructed apparatus are mostly used for this purpose, those which, owing to their convenient form, compactness, and simplicity of manipulating, are most frequently met, will be briefly described in the following articles.

52. Modified Elliott Apparatus.—The modified Elliott apparatus shown in Fig. 18 consists of two glass tubes: *i b*, which has a capacity of about 120 to 130 cubic centi-

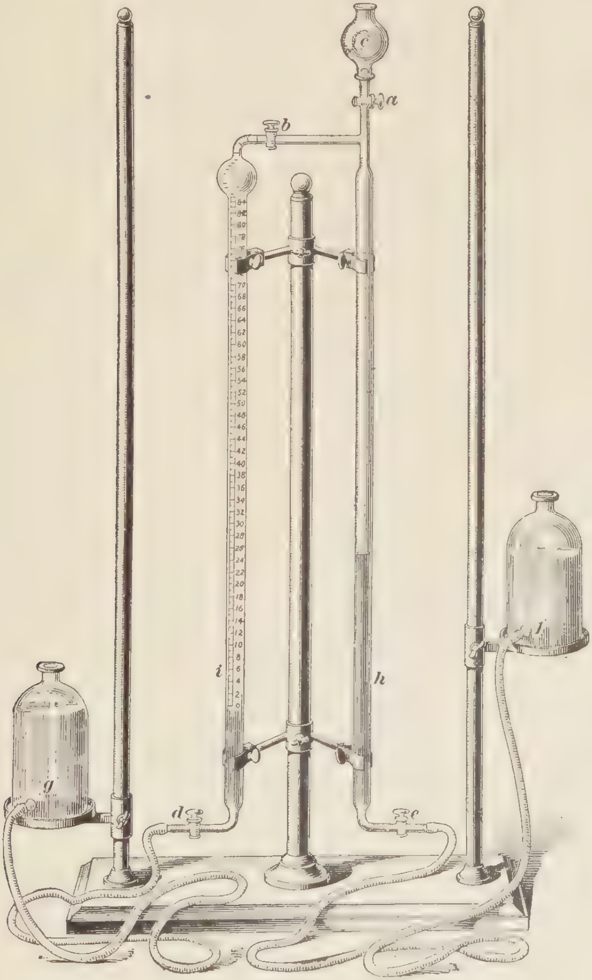


FIG. 18

meters and which is accurately graduated from 0 to 100 cubic centimeters in one-tenth cubic centimeters, and the ungraduated tube *a h*. At *d* and at *e*, a three-way glass

stop-cock connects each of these tubes with a water-supply bottle. The bottles are shown at *g* and *f*.

53. Manipulation of the Apparatus.—The manipulation of the apparatus is as follows: The funnel cap *c* is removed and in its place is connected a glass tube of small diameter; this tube must be of sufficient length to reach well into the flue from which the gas to be analyzed is taken. The stop-cocks *a* and *b* are opened, and the water-supply bottles *f* and *g* are slowly raised until both tubes as well as the glass tube that leads into the flue are filled with water, care being taken that no air remains in the tubes, and that the displacement of water is complete. The cock *b* is closed. The bottle *f* is now gradually lowered, which causes the tube *a h* to be filled with gas.

As soon as sufficient gas has been obtained for the analysis, the lower portion of the tube containing water 2 or 3 inches above the point *h*, the stop-cock *a* is closed, the small glass tube reaching into the flue disconnected, and the cap *c* replaced. After the gas is allowed to remain in the tube *a h* for about 15 minutes, to adjust its temperature to that of the room, and thus insuring accurate measurement, the bottle *g* is slowly lowered until the surface of water therein is on an exact level with zero mark on the tube *i b*; the stop-cock *b* is then opened and the bottle *f* gradually raised until a sufficient quantity of gas has been transferred from *h a* to *i b*, which will be indicated by the volume taken, reading from the mark *0* on the graduated tube *i b* to the mark *100* immediately in contact with the stop-cock *b*.

Having thus obtained 100 cubic centimeters of the gas, the stop-cock *b* is closed and *f* is raised until all the remaining gas in *a h* and *a b* is displaced by the water. The first constituent of the gas to be determined is carbon dioxide. The gas is transferred to the tube *a h* by raising *g* and opening *b*, keeping *a* closed and *f* lowered. When the water reaches *b*, the latter is closed. In the funnel cap *c* are placed 50 cubic centimeters of caustic potash. This solution is made by dissolving 280 grams of potassium hydrate in 1,000 cubic

centimeters of distilled water. The stop-cock *a* is partially opened, so that the potassium-hydrate solution in *c* may slowly drop down through the gas in the tube *h* and absorb the carbon dioxide in doing so.

When all but 2 or 3 cubic centimeters of the potassium-hydrate solution has passed through *a*, the latter is closed, thus preventing entrance of any air; *b* is opened, *f* is slowly raised, and *g* lowered. The raising of *f* is continued until the water in the tube *h a* reaches the stop-cock *b* and the latter is immediately closed. The gas is allowed to stand in the tube *i b* five minutes before taking the reading of the volume on the tube, bearing in mind that the level of the water in *g* must be on a level with the water in *i b* to obtain equal pressure. The difference between *0* and the point indicated by the water in the tube *i b* will give the amount of carbon dioxide absorbed from the gas by the potassium-hydrate solution.

Thus original volume indicated	=	0.0
After absorption of CO_2	=	12.1
Carbon dioxide	=	12.1, or 12.1% carbon dioxide by volume.

To obtain the oxygen, the gas is transferred from *i b* to *a h*, as described before, and in *c* is placed 50 cubic centimeters of an alkaline solution of pyrogallol. A suitable solution is prepared by dissolving 10 grams of pyrogallol in 25 cubic centimeters of distilled water, placing it in *c*, and adding 35 cubic centimeters of the potassium-hydrate solution. This is allowed to pass slowly through *a* and gradually absorbs the oxygen in the gas; *a* is closed before all the liquid passes out of *c*. The operation is once repeated, and the gas transferred in the usual manner to *i b*, where it is measured after it has been resting there for 5 minutes.

Previous reading	=	12.1
After absorption of O	=	18.5
Oxygen	=	6.4, or 6.4% oxygen by volume.

Before transferring the residual gas to *a h* for the determination of the carbon monoxide, all the water in *f* and *a h*

must be replaced by fresh distilled water; to do this, the three-way cock *e* and *a* are opened, when the water will run out of *e* and may be caught in a beaker; *f* and *a h* are thoroughly washed 2 or 3 times with water; *e* is closed in such a way that connection with *f* is again established; *f* is filled with fresh water and raised, and, when the tube *a h* is filled up to *a*, the latter is closed and *f* lowered; *g* is then raised and *b* opened, thus transferring the gas to *a h* for treatment with a solution of cuprous chloride to determine CO.

A suitable cuprous-chloride solution is prepared by dissolving 30 grams of cuprous chloride in 200 cubic centimeters of hydrochloric acid (Sp. Gr. 1.19) and using 50 cubic centimeters of it, as soon as the solution has approximately obtained the temperature of the room. Experience has shown that a freshly prepared solution is much more effective as an absorbent of CO than one that has been standing for some days. In *c* are placed 50 cubic centimeters of this solution, and it is allowed to slowly drop through *a* and absorb the CO as it passes through the gas. This absorption should be repeated 2 or 3 times. The heat generated during this absorption often causes such an increase in the volume of the gas that, when the latter is transferred to the measuring tube, inaccurate readings are obtained. To insure accuracy, the following should be observed:

The gas, after fifteen minutes, is transferred in the usual way to *b i* and the water in *f* and *a h* is replaced by fresh water. The gas is then returned to *a h* and a solution of potassium hydrate is placed in *c* and allowed to drop through the gas in *a h*, absorbing all traces of hydrochloric gas. This process is once repeated, the gas returned to *b i*, and, after allowing it to stand for 15 minutes, the volume is accurately measured.

Previous reading	= 18.5
After absorption of CO	= 20.0
Carbon monoxide	= 1.5 or 1.5% carbon monoxide.

The nitrogen present is obtained, as in previous experiments, by difference.

Thus, the analysis will read:

Carbon dioxide	=	12.1
Oxygen	=	6.4
Carbon monoxide	=	1.5
Nitrogen	=	80.0
Total	=	100.0

In this analysis, no corrections are required for the tension of the aqueous vapor, since the original gas is saturated with moisture, and, during the analysis, all measurements are made over water.

54. Orsat-Muenke Apparatus.—In the writer's opinion, the apparatus that is best adapted for the rapid determination of carbon dioxide, oxygen, and carbon monoxide is the *Orsat-Muenke;* it is readily portable, not liable to be broken, easy to manipulate, sufficiently accurate for all technical purposes, and always ready for use.

The apparatus, shown in Fig. 19, consists of the graduated measuring burette *a*, of 100 cubic centimeters capacity; it is jacketed with water, to prevent changes of temperature affecting the gas volume; the first 45 cubic centimeters are usually divided into one-tenth cubic centimeters, while the remaining 55 cubic centimeters are divided into cubic centimeters only. The burette ends in a thick capillary tube, which is fastened at both ends, at *b* in a cut of the dividing panel, and at *c* by means of a small brace attached to the cover of the case. The capillary tube is bent at its further end and connected with the U tube *d* containing some loose cotton, and at the bend is filled with water in order to retain all dust and to saturate the gas thoroughly with moisture before measuring takes place. The rear end of the three-way cock *e* is connected by means of a rubber tube *f* with the rubber aspirator *g*, which fills the tube with the gas to be analyzed. The absorption of the different constituents of the gas under examination takes place in the U-shaped absorption pipettes *h*, *i*, and *j*, which are connected with the stoppers by short rubber tubes. For the enlargement of the

absorbing surfaces, *h*, *i*, and *j* are filled with glass tubes. Since the mark *k* is above the place of connection, the latter is always moistened by the respective liquid, and, therefore,

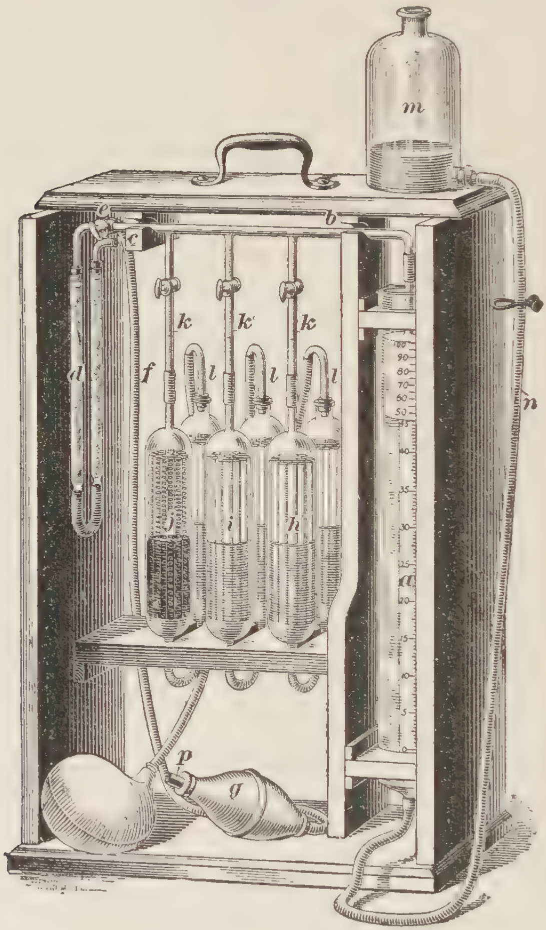


FIG. 19

can easily be maintained air-tight. The other end of the absorption pipettes is closed by a rubber cork, which contains the small tube *l*; the small tubes are all connected to one rubber bulb of about 200 cubic centimeters capacity, in

order to keep out the atmospheric oxygen. The entire apparatus is enclosed in a wooden case.

55. Charging the Orsat-Muenke Apparatus.—The glass jacket surrounding the burette *a*, as well as the bottle *m*, is filled with distilled water. In order to fill the three absorption pipettes, the stoppers are removed, as well as the glass tubes *l* and the rubber aspirator *g*, and 110 cubic centimeters potassium-hydrate solution, Sp. Gr. 1.26, are poured into the pipette *h*, so that the latter is about half full. This is for the absorption of CO_2. The pipette *i* contains a solution of 18 grams of pyrogallol in hot water, which is poured into it, and then 70 cubic centimeters of potassium-hydrate solution, Sp. Gr. 1.26, are added, whereby the oxygen is absorbed in the gas under examination. The carbon monoxide is absorbed in the pipette *j*, which contains a solution of cuprous chloride made as follows: 35 grams of cuprous chloride are dissolved in 200 cubic centimeters of concentrated hydrochloric acid, 50 grams of copper clippings added, and the mixture allowed to stand in a glass-stoppered bottle for 24 hours.

Each glass tube in *j* contains a spiral of copper wire. To this solution is added 100 cubic centimeters of water, and enough is transferred to *j* to fill it to the required point. The solutions in the rear section of *h*, *i*, and *j* are transferred to the front part of the pipettes, where the absorption of the gases takes place as follows: The three glass stoppers are closed, the stop-cock *e* turned horizontal, and the bottle *m* containing distilled water raised so that the water fills the burette *a*; give a quarter-turn to the left to the stop-cock *e*, so that the second passage leads to the tube *d*, open the stop-cock of the absorption pipette *h*, lower the bottle *m*, and carefully open the pinch cock placed on the tube *n*, so that the potassium-hydrate solution rises to the mark *k*, whereupon the stop-cock is closed.

The reagents of the two other absorption pipettes are raised in an exactly similar way to *k*. The three stoppers with glass tubes *l* are then attached. About 1 cubic centimeter

of water is placed in the tube *d*, loose cotton is placed in both sides, the stopper reinserted and again connected. After filling the burette *a* with water to the 100-cubic-centimeter mark by raising the bottle *m*, the stop-cock is turned so that the connection of the rubber aspirator *g* with the chimney containing the flue gases is brought about through the tube *p*. Aspiration of the gas into the apparatus is now performed by compressing *g* 10 to 15 times, until the whole conductor is filled with gas. This is easily done by compressing *g* with the left hand, closing the attached tube *f* with the thumb of the right hand, and then, on opening the left hand, allowing *g* to expand, raising the thumb again, compressing *g*, etc., until the object is obtained. To fill the burette *a* with the gas, the stop-cock *e* is turned horizontal, the pinch cock of the tube *n* opened, and the bottle *m* lowered until the gas reaches the zero point in *a*, whereupon *e* is closed.

56. Manipulation of the Orsat-Muenke Apparatus. To determine the carbon dioxide, the stop-cock of the absorption pipette *h* is opened and *m* raised with the left hand, so that on opening the pinch cock of *n* with the right, the gas enters *h*; *m* is lowered again until the potassium-hydrate solution in *h* reaches to about the tube connection under *k*, and once again drives the gas into the potassium-hydrate vessel by raising *m*. This is repeated 2 or 3 times, and the gas returned to the burette *a* by opening the pinch cock of *n*, lowering *m*, and closing the stop-cock of *h*. To measure the amount of absorbed carbon dioxide, the bottle *m* is held next to the burette in such a way that the water stands at the same level in both vessels, the pinch cock of *n* is closed, and the remaining volume of the gas read off. This amount, subtracted from 100 cubic centimeters, gives the amount of CO_2.

The gas is then passed into the pipette *i* in the same manner as in *h*, the oxygen being absorbed by the alkaline pyrogallate solution. This absorption is repeated 3 or 4 times, and the gas returned to the measuring tube, and the

amount of absorption read off. The gas is then passed into the pipette *j* for the absorption of carbon monoxide. After repeating for a number of times the absorption in *j*, the gas is passed into *h* before measurement in *a* of the absorbed carbon monoxide. This is necessary on account of the vapors of hydrochloric acid retained by the gas after contact with the cuprous-chloride solution in hydrochloric acid. After passing the gas into *h* 3 or 4 times, it is then measured as usual in *a*, the residual gas being nitrogen.

ANALYSIS OF URINE

PRELIMINARY REMARKS

57. A complete analysis of urine is seldom, if ever, required, and, as in the case of water, only certain constituents are determined. Some of these constituents are never present in normal urine, but occur in the urine of patients suffering from certain diseases; hence, the mere presence of these constituents is sufficient to prove the disease, and a qualitative examination serves this purpose. But even in these cases, the quantities of such constituents are required to indicate the progress of the disease, and, consequently, a quantitative examination is necessary. Other constituents are always present in urine, and, in these cases, qualitative determinations would, of course, be useless. The indications obtained in these cases depend on the quantities of these constituents present, and, consequently, a quantitative examination is required. Certain qualitative determinations are sometimes valuable in examining urine, and, consequently, the subject was partially treated in *Qualitative Analysis*, Part 2. All the determinations given there may be used in examining any sample, and the determinations of color, reaction, and specific gravity, which are always made, need not be repeated at this point.

58. Selecting a Sample.—As the total amount of each constituent passed in 24 hours is what a physician ordinarily wants to know, and as the composition of the urine varies greatly at different times during the day, the selection of the sample for analysis becomes a matter of importance. Ordinarily, the best method of obtaining a sample is to collect the total amount passed during the 24 hours. The volume of this should be carefully noted, the whole thoroughly mixed, and then samples taken for the different determinations. Then, knowing the total amount passed, and the amount taken for the determination of each constituent, the quantity of each constituent passed in 24 hours is readily calculated.

The results obtained in examining a sample passed at one time may be misleading, both because the total amount passed is not taken into account, and because the composition of the urine examined may not represent the composition of the whole. A sample passed at another time during the day might contain only half, or might contain double, the amount of a constituent that is contained in this sample. Then, if the total amount of urine passed is not known, we have nothing from which to calculate the quantity of each constituent passed. The amount of urine passed in 24 hours is frequently given as ranging from 1,200 to 1,500 cubic centimeters, but cases have fallen under the writer's observation in which the total amount passed in 24 hours was rather less than 600 cubic centimeters; while, in others, more than 2 liters were passed during the 24 hours. Results calculated on a basis of 1,200 or 1,500 cubic centimeters, in any of these cases, would obviously have been misleading.

While this method of taking a sample should usually be followed, circumstances frequently demand that it be modified in order to obtain more complete knowledge than would be afforded in this way. For instance, samples of urine passed shortly after a meal are sometimes alkaline; while, at other times, the reaction is acid. To learn this, samples passed at different times during the day would need to be tested separately. Sometimes when urine contains a very small

amount of albumin, a sample passed on rising in the morning will not reveal a trace of this substance, but a sample passed a short time after a meal will give a distinct reaction for this constituent, and the same may be said of minute quantities of sugar. The best plan in such cases is to examine two samples, one passed about an hour after dinner and the other passed on rising in the morning.

Whatever method of collecting a sample is employed, it should be remembered that urine decomposes quite rapidly on standing, especially in a warm place; hence, the sample should be kept in a cool place, and should be examined as soon as possible after it is collected. The chemist's duty ends with the accurate determination of the various constituents, and the interpretation of the results obtained falls within the province of the physician; hence, the pathological significance of the different constituents will not be discussed here.

The principal determination made in the examination of urine are color, reaction, specific gravity, sugar, albumin, urea, uric acid, and chlorides. The total quantity passed in 24 hours should also be noted. As the total amount passed in 24 hours is learned by merely keeping all that is passed and measuring it in a graduated vessel, and as the determinations of color, reaction, and specific gravity have already been fully described in *Qualitative Analysis*, it is unnecessary to further treat these determinations here, and we will consequently pass on to the description of the others.

SUGAR

59. A careful qualitative test for sugar should first be made, and if this shows that the urine is free from sugar, the quantitative determination is, of course, omitted. If, however, sugar is found to be present, the next step is to determine its quantity. The quantitative estimation of sugar is accomplished by means of Fehling's solution, but when this is to be used for quantitative determinations, greater care is required in making up the copper solution. Strictly pure

copper-sulphate crystals that have not lost water of crystallization to the amount of 34.639 grams are dissolved in water and diluted to 500 cubic centimeters; 173 grams of Rochelle salts and 125 grams of potassium hydrate are dissolved in water and diluted to 500 cubic centimeters.

60. Determination of Sugar.—When ready to make a determination, thoroughly mix exactly 10 cubic centimeters of the copper-sulphate solution, and an equal amount of the alkaline solution of Rochelle salts. A portion of this solution may be used for the qualitative test. Then measure exactly 2 cubic centimeters of the solution just prepared into a small flask, dilute it to 10 cubic centimeters, and boil it for 15 or 20 seconds, to see that it does not decompose. If it remains clear, add a few drops of a dilute solution of glucose or honey, and again bring the solution to the boiling point, to see if a precipitate forms promptly, thus testing the solution. If the solution decomposes when boiled, or if a red precipitate is not formed when the glucose is added, there is something wrong with the solution, and a new one must be prepared. This will never happen if pure materials are used, and the solution properly made up.

When a solution is obtained that does not decompose on boiling and that gives a precipitate when a few drops of glucose solution are added, rinse out the flask thoroughly, introduce exactly 2 cubic centimeters of the Fehling solution, and dilute it to 10 cubic centimeters with distilled water. Place the flask on a gauze over a burner, and, as soon as the contents commence to boil, remove it, and add a little of the urine under examination from a burette. The amount of urine that it is safe to add at first will be indicated by the qualitative test. Heat the solution just to boiling, remove it from the heat immediately, give it a rotary motion to secure thorough mixing, allow the precipitate to partially settle, and note the depth of the blue color of the solution. Then continue the addition of urine, a little at a time, bringing the solution just to the boiling point after each addition, until the blue color of the solution is just discharged. From

the amount of urine added to just decolorize the solution, calculate the percentage of sugar in the sample.

The calculation is based on the fact that the 2 cubic centimeters of Fehling's solution used are reduced by .01 gram of sugar; hence, the volume of urine required to decolorize the solution contains .01 gram of sugar. As the specific gravity of urine is never very much greater than 1, it is generally assumed in making this calculation that the specific gravity of the sample is 1, or, what is the same thing, that 1 cubic centimeter of it weighs 1 gram. This is never exactly correct, but is sufficiently accurate for practical purposes. Using this as a basis of calculation, if 1 cubic centimeter of the urine is required to discharge the blue color, the sample contains 1 per cent. of sugar; if .5 cubic centimeter is required, the sample contains 2 per cent. of sugar; and if 2 cubic centimeters are required, the solution contains .5 per cent. of sugar. If more accurate results are required, the specific gravity of the urine must be taken into account.

This titration is, in a sense, the reverse of any so far performed, inasmuch as the reagent is measured out, and the sample added; hence, the greater the amount of sample added from the burette, the lower the percentage of sugar indicated. If a sample contains much sugar, it is best to measure exactly 10 cubic centimeters of it into a graduated 100-cubic-centimeter flask, dilute it exactly to the mark with distilled water, and use this diluted sample for the determination. In this case, an appropriate calculation must, of course, be made in reckoning the result.

ALBUMIN

61. Albumin occurs in the urine of patients suffering from certain diseases of the kidneys, and the qualitative methods that have been given in *Qualitative Analysis* are sufficient to indicate these. But, in many cases, it is important that the physician should know the relative amount of albumin contained in the urine from day to day, and, for this purpose, quantitative methods are required. At present,

we have no very satisfactory method for the quantitative determination of albumin. Probably the most accurate one is the gravimetric method, in which the albumin is precipitated by heating the sample and adding an acid; but this method is long and troublesome, and the results obtained by one of the shorter approximate methods are frequently accurate enough for practical purposes. Two methods frequently used are here given.

62. Gravimetric Determination.—Measure 100 cubic centimeters of the sample into a beaker, stand it on a gauze over a burner, and, just as it begins to boil, add 10 or 12 drops of nitric acid of 1.2 Sp. Gr. Mix the solution, cover the beaker with a watch glass, allow it to stand undisturbed for at least 12 hours, and then filter through a paper that has been dried at 100° and weighed. Wash the precipitate and filter thoroughly, dry at 100° until a constant weight is obtained, and, from the weight obtained, calculate the percentage of albumin in the sample.

Acetic acid is frequently used instead of nitric acid to precipitate the albumin, and in some ways it is preferable; but in some cases it forms a slimy precipitate that it is almost impossible to filter. The method is tedious at best, and the following method, which yields approximate results, is usually sufficiently accurate for the purpose of comparison:

FIG. 20

63. Determination With Esbach's Albuminimeter.—In using **Esbach's albuminimeter,** the albumin is precipitated by an acid mixture and the percentage is indicated approximately by the size of the precipitate. The albuminimeter is simply a graduated tube shown in Fig. 20. To make the determination, fill the tube to the mark *U* with the urine to be tested, then add the Esbach reagent to bring the liquid to the mark *R* when the tube is standing in an upright position. Close the tube with the rubber stopper provided

for the purpose, cautiously mix the contents, and allow the tube to stand, undisturbed, in an upright position for 24 hours. The albumin will be coagulated by the acid reagent, and will settle to the bottom of the tube, so that the amount present may be read off.

In mixing the urine and reagent, place the stopper in the tube and slowly invert it, then bring it back to an upright position, and repeat this 10 or 12 times, but do not shake or agitate the liquid violently. Each graduation line at the bottom of the tube indicates 1 gram of albumin in a liter of urine. For example, if the precipitate of albumin reaches to the second line from the bottom, it indicates that 1 liter of the urine contains 2 grams of albumin, or that the sample contains .2 per cent. of this constituent. Knowing the amount of albumin in a liter, and the total amount of urine passed, the amount of albumin passed in 24 hours is readily calculated.

The urine used for this determination should have an acid reaction, and, as albuminous urines are sometimes neutral or even alkaline, the reaction should always be determined before this estimation is commenced. If the urine is found to be neutral or alkaline, pour approximately the amount needed for the determination into a beaker and add acetic acid, drop by drop, while stirring the sample, until a drop of the urine, removed on the stirring rod and brought in contact with blue litmus paper, imparts a red color to it; but avoid a large excess of the acid. More than 3 drops of the acid will seldom be required. This acidulated sample is used for the determination.

The results obtained by this method are more accurate and concordant when only small quantities of albumin are present. Consequently, when the qualitative test indicates a large amount of albumin, it is best to dilute a portion of the sample with distilled water. The amount of water to be added will depend on the amount of albumin in the urine. It is best to dilute the sample until it contains less than 5 grams per liter of albumin. Of course, an appropriate calculation must be made in obtaining the result, in case the sample is diluted in this way.

Esbach's solution, used to precipitate the albumin, is made by dissolving 10 grams of picric acid and 20 grams of citric acid in distilled water, and diluting the solution to 1 liter. The picric acid is to coagulate the albumin, and the citric acid to hold the phosphates in solution. The solution should be kept in a tightly stoppered bottle. As this method only gives approximate results at best, it should be carefully performed. The solution should always be allowed to stand just 24 hours before taking the reading.

UREA

64. As **urea** is the most abundant solid constituent of urine, and is always present, a qualitative examination for this constituent is never required, but its quantitative estimation is frequently a matter of importance. Methods based on two different principles are largely employed for its determination. The volumetric method proposed by Liebig was used almost exclusively until recently. This method depends on the fact that mercuric nitrate precipitates urea quantitatively. Recently, it has been largely superseded by a process in which the urea is decomposed by an alkaline solution of hypobromite and the nitrogen evolved measured.

A number of forms of apparatus for carrying out this process have been suggested by different chemists. The forms devised by Hüfner and Doremus are described here. It has been objected to the hypobromite process that the results obtained by it are too low, and this is true if the results are calculated from the theoretical composition of urea; but as the results are usually calculated from the amount of nitrogen found by experiment to be liberated by a given weight of urea, this objection will scarcely hold good. At all events, the results obtained by this process are sufficiently accurate for practical purposes. The older process will be described first.

65. Liebig's Method.—For this method, we need a standard solution of mercuric nitrate of such strength that

1 cubic centimeter is exactly equivalent to .01 gram of urea, a saturated solution of pure sodium carbonate, and a barium solution made by mixing 1 volume of a cold saturated solution of barium nitrate with 2 volumes of a cold saturated solution of barium hydrate. A standard solution of mercuric nitrate, made by dissolving 77.2 grams of pure mercuric oxide in nitric acid and diluting to 1 liter with water, will be of the proper strength for use. It is prepared as follows:

Dissolve 78 grams of mercuric oxide in nitric acid; by the aid of heat, evaporate the solution to a syrupy consistency over a water bath, and dilute this syrupy liquid to somewhat less than 1 liter with distilled water. If a precipitate of basic nitrate separates when the water is added, allow it to settle and decant the clear liquid. Then dissolve the precipitate in the least necessary quantity of nitric acid; add this to the main solution, and mix the whole thoroughly, and standardize it against a urea solution of known strength.

For this purpose, dissolve 2 grams of pure urea in distilled water, dilute it to exactly 100 cubic centimeters, and mix it thoroughly. A solution is thus obtained 10 cubic centimeters of which contain .2 gram of urea. Measure exactly 10 cubic centimeters of this solution into a beaker, and slowly introduce the mercuric nitrate solution from a burette while stirring constantly. As the mercuric nitrate falls into the urea solution, it produces a dense precipitate. When the precipitation seems to be nearly complete, remove a drop of the solution from the beaker on a stirring rod, and bring it in contact with a drop of the saturated solution of sodium carbonate placed on a suitable surface. Some chemists use a *spot plate* or porcelain slab for this purpose, while others prefer a piece of glass standing on a black ground.

If the urea is not completely precipitated, there will be no change of color. Continue to add the mercuric nitrate cautiously, testing after each addition, until a yellow color is produced when a drop of the solution is brought in contact with a drop of the sodium carbonate. This indicates that the urea is completely precipitated, and that the solution

contains a trace of mercuric nitrate, which reacts with the sodium carbonate. Note the reading of the burette, and, from this, calculate how much the solution must be diluted. Add water to the solution until, after thorough mixing, just 20 cubic centimeters of it are required to precipitate the urea in 10 cubic centimeters of the solution and give a faint yellow tinge to a drop of sodium carbonate. The solution will now be of such strength that 1 cubic centimeter of it represents .01 gram of urea.

Having, now, an accurately standardized solution of mercuric nitrate, we are prepared to determine the urea in a sample of urine. This is accomplished as follows: Measure exactly 40 cubic centimeters of the urine into a beaker, add 20 cubic centimeters of the barium solution, and stir thoroughly. The barium solution precipitates the sulphates, carbonates, and phosphates. Filter through a dry filter placed in a dry funnel, and receive the filtrate in a dry, clean beaker. If a good quality of filter paper is used, the filtrate should be clear, but if cloudy, it should be passed through the paper a second time. Measure into a beaker 15 cubic centimeters of the filtrate, which, of course, will contain 10 cubic centimeters of the urine, and add standard mercuric nitrate solution from a burette until a drop of the solution, when brought in contact with a drop of sodium carbonate, produces a yellow color of the same depth as that obtained in standardizing the mercuric nitrate solution.

From the quantity of standard mercuric nitrate used, calculate the percentage of urea in the sample, or the amount passed in 24 hours. With normal urine, the specific gravity serves as a guide in making the titration. A number of cubic centimeters of mercuric nitrate approaching the last two figures of the specific gravity, may usually be added before testing for the end of the reaction. Thus, if the specific gravity of the urine is 1.020, it is generally safe to add 18 cubic centimeters of mercuric nitrate before mixing a drop of the solution with sodium carbonate.

The results obtained by this method are usually correct enough for practical purposes, but their accuracy may be

increased by certain corrections and modifications. Those frequently applied are as follows:

If the urine contains more than 1 per cent. of sodium chloride, 2 cubic centimeters are deducted from the total quantity of mercuric nitrate required to produce the yellow color with sodium carbonate before the calculation is made. It has been found by experiment that about this amount of the mercuric solution is used up by the sodium chloride. If still greater accuracy is required, the chlorine is first determined, just enough silver nitrate is added to precipitate it in the sample used, and the silver chloride is filtered off before the barium solution is added. This is a rather troublesome process, however, and is seldom resorted to.

If the urine contains more than 2 per cent. of urea, that is, if more than 20 cubic centimeters of mercuric nitrate are required for its precipitation, a second sample must be titrated after adding to it half as much water as there was mercuric nitrate required in excess of 20 cubic centimeters in the first titration. For instance, if 26 cubic centimeters of mercuric nitrate are added to the first sample, this would be 6 cubic centimeters in excess of 20, and, consequently, 3 cubic centimeters of water must be added to the second sample before titrating it.

If the urine contains less than 2 per cent. of urea, .1 cubic centimeter is subtracted from the total for each 4 cubic centimeters less than 20 of the mercuric nitrate solution used. Thus, if 12 cubic centimeters of mercuric nitrate are required, 8 cubic centimeters less than 20 are used, and, consequently, .2 cubic centimeter must be deducted; hence, 11.8 cubic centimeters of mercuric nitrate should be taken in making the calculation.

If much albumin is present, it interferes with the titration, and should, consequently, be removed. This is done as follows: Measure out exactly 50 cubic centimeters of the urine, add 2 drops of strong acetic acid, and boil the solution a few moments to coagulate the albumin. After allowing the precipitate to completely settle, decant exactly 30 cubic centimeters of the clear solution, add 15 cubic centimeters

of the barium solution, filter off the precipitate, and proceed with the determination as usual. If the precipitated albumin remains at the bottom of the vessel, 40 cubic centimeters of the clear liquid may be decanted and mixed with 20 cubic centimeters of the barium mixture.

66. Determination With Hüfner's Apparatus.—For this determination, we need an alkaline solution of sodium hypobromite. It is made by dissolving 100 grams of sodium hydrate in 250 cubic centimeters of distilled water, and slowly stirring in 25 cubic centimeters of bromine, when sodium hypobromite is formed according to the equation:

$$2NaOH + Br_2 = NaBr + H_2O + NaBrO$$

Hüfner's apparatus is shown in Fig. 21. The lower bulb *a*, which is fitted into a wooden support, is connected with the bulb *c* by means of a tube containing the stop-cock *b*. The upper part of the bulb *c* is drawn out to a tube, the exterior of which is of ground glass. The perforated glass vessel *d* fits over this tightly, and the graduated tube *e* fits over it loosely inside of the vessel *d*.

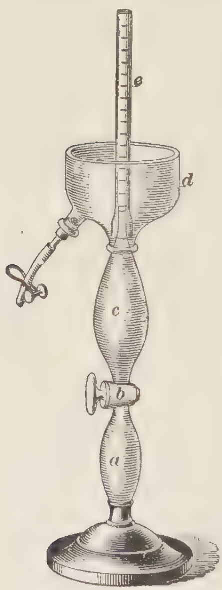


FIG. 21

To determine the urea by means of this apparatus, measure accurately about 2 cubic centimeters of the urine into the bulb *a*, and fill this to the top of the stop-cock with freshly distilled water. Close the connection between the two bulbs by turning the stop-cock, and fill the bulb *c* with equal parts of hypobromite solution and freshly distilled water. Fit the vessel *d* over the tube of the bulb *c*, making sure that the connection is tight, and pour in enough distilled water to cover the end of the tube. Then fill the graduated reading tube with distilled water, and invert it over the tube at the top of the bulb *c*, as shown in the figure. Be sure that the apparatus contains no air bubbles. Now

turn the stop-cock *b*, and allow the hypobromite and urine to mix. The hypobromite immediately attacks the urea, liberating carbon dioxide and nitrogen according to the equation :

$$CO(NH_2)_2 + 3NaBrO = 3NaBr + 2H_2O + CO_2 + N_2$$

The carbon dioxide is absorbed by the excess of sodium hydrate in the hypobromite solution, and the nitrogen collects in the reading tube *c*. When the reaction is complete, and the gas has all collected in the reading tube, transfer this to a vessel of water that has been standing in the room for some time, to acquire its temperature, taking care not to allow any air to enter the tube. After suspending it in this water for a few minutes, bring the level of the water in the tube to the level of that on the outside, and carefully note the volume of nitrogen when the pressure is thus equalized. Then immediately note the temperature and barometric pressure. The urea is then calculated by the formula:

$$W = \frac{100\ v\,(P-p)}{760 \times 354.33\, a\,(1+.00366\, t)}; \qquad \textbf{(5)}$$

in which

W = weight, in grams, of urea in 100 cubic centimeters of the urine;

a = volume of urine taken;

v = volume of nitrogen obtained, in cubic centimeters;

t = observed temperature, in centigrade degrees;

P = observed barometric pressure, in millimeters;

p = tension of aqueous vapor for the temperature t.

Having now the weight of urea in 100 cubic centimeters of the urine, the amount passed in 24 hours, or the percentage, is readily calculated. In calculating the percentage of urea, the weight of 100 cubic centimeters of urine is of course obtained from the specific gravity of the sample. In handling the reading tube containing the nitrogen, care should be exercised to avoid touching it with the hands more than is necessary, as the warmth of the hand is sufficient to expand the gas and thus cause an error.

It has been found that when the vessel *d* contains water,

the water passing out of the reading tube sometimes carries nitrogen with it, and this is allowed to escape. To avoid this loss, a solution of salt is frequently placed in *d*, instead of water.

67. Estimation With Doremus's Apparatus.—For the determination of urea with the Doremus apparatus, pure bromine and a solution of sodium hydrate are required. The sodium-hydrate solution is made by dissolving 100 grams of the solid in 250 cubic centimeters of water. The apparatus is shown in Fig. 22. It consists of a bulb and tube, and a small, curved, nipple-capped pipette, graduated to measure 1 cubic centimeter. The tube of the apparatus is so graduated that each of the small divisions represents .001 gram of urea. On the side of the tube opposite the graduation, two parallel lines are drawn close to each other. To use this ureameter, pour in enough of the sodium hydrate to fill the graduated tube to the parallel lines, then, by means of the nipple pipette, add 1 cubic centimeter of bromine, and when this has completely dissolved, add water to fill the graduated tube and bend up to the bulb.

FIG. 22

Mix the solution in the apparatus, and wash the pipette thoroughly. Draw up exactly 1 cubic centimeter of the urine in the pipette, pass the curved end of it through the bulb of the ureameter as far as it will go in the bend, and, by pressing gently and steadily on the nipple, force the urine out into the graduated tube, which is held in a perpendicular position. As soon as all the urine is expelled, withdraw the pipette, taking care not to press the nipple sufficiently to force air out after the urine. When the urine comes in contact with the hypobromite solution, the urea is decomposed the same as in the Hüfner apparatus;

occupied thereby is assumed to be a little more than 1 cubic centimeter. Since it is advisable to have as large a volume as convenient, Pellet recommends to wash the pulp into a flask graduated at 201.35 cubic centimeters. If a 200-cubic-centimeter flask is used, the weight of the pulp should be 25.87 grams instead of 26.048 grams. After the pulp is washed into the flask, about 6 cubic centimeters of lead acetate, having a specific gravity of 30° Baumé, are added together with a little ether, to remove the foam. The flask is now gently shaken and water added to the mark, and the contents thoroughly shaken up. If the pulp has been rasped or grated finely enough, the filtration and polarization may follow immediately. The filter into which the contents of the flask are poured should be large enough to hold the whole quantity at once. If 26.048 grams have been taken, the volume diluted to 201.35 cubic centimeters, and the liquid polarized in a 200-millimeter tube, the percentage of sugar can be read off directly.

It is not necessary to heat the solution in order to insure complete diffusion, but the temperature at which the operation is conducted should be the ordinary one of the laboratory. In case the pulp is not as fine as it should be, the flask should be allowed to stand for half an hour after filling, before filtration. An insufficient amount of lead acetate may permit some rotary bodies other than sugar to pass into solution, and care should be taken always to have the proper quantity of the clarifying material added.

109. Analysis of Beet Juice.—The beet under examination is grated on an ordinary grater and about a pint of the pulp placed in the cylinder of the press shown in Fig. 19. Pressure is applied, and the thus extracted juice flows into a beaker under the spout. The juice is then poured into a tall cylindrical glass, its temperature noted, and the density observed by means of a Brix hydrometer. Of this juice, 100 cubic centimeters are then transferred by means of a pipette to a sugar flask having two graduations, one at 100 cubic centimeters and one at 110 cubic

health, it is found in quantities ranging from .4 to .8 gram in 24 hours, and usually varies with the urea, of which it is one stage short in oxidation.

Several volumetric methods for the estimation of uric acid have been proposed, but they are all long and cumbersome, and apparently liable to error; hence, the *gravimetric method* is usually employed.

69. Gravimetric Determination of Uric Acid. Measure 200 cubic centimeters of the sample into a beaker, add 20 cubic centimeters of hydrochloric acid, mix thoroughly, cover the beaker with a watch glass, and stand it in a cool place for 30 hours. During this time, the uric acid will separate, and will be found in crystals at the bottom of the beaker, and on the sides, adhering to the glass. Filter on a paper that has been dried at a temperature ranging from 100° to 105° and weighed, removing the last of the crystals from the beaker by means of a "policeman." Wash thoroughly with distilled water, and note the volume of the filtrate and washings. Place the filter containing the precipitate in an air bath, and heat it at a temperature ranging from 100° to 105° until a constant weight is obtained. It should be dried for 1 hour at this temperature before making the first weighing. To the weight of uric acid thus obtained, add .0038 gram for each 100 cubic centimeters of filtrate and washings, and, from the weight thus obtained, calculate the percentage of uric acid, or the amount passed in 24 hours.

Neubauer finds that 100 cubic centimeters of the filtrate and washings retain .0038 gram of uric acid, and, consequently, advises the addition of this weight for each 100 cubic centimeters of solution in the filtrate, as directed above.

CHLORIDES

70. Chlorine exists in urine chiefly in the form of sodium chloride, but also, in smaller quantities, combined with potassium and ammonium. As most of the chlorine is combined with sodium, it has become customary to calculate it

all to sodium chloride, and report it as such. There are a number of methods for the determination of chlorine in urine, but the one that appears to be the most satisfactory and is most largely employed is the volumetric method devised by Mohr. The details of this process are as follows:

71. Mohr's Method.—Measure 10 cubic centimeters of the sample into a platinum crucible, dissolve from 1 to 2 grams of pure potassium nitrate in it, and slowly evaporate to dryness. Then gradually increase the temperature until the organic matter in the residue is completely burned and a white mass remains, but avoid sudden or long-continued heating, lest chlorine be expelled. Dissolve this saline mass in a little distilled water, wash the crucible with a jet of water from a wash bottle, and allow the washings to run into the beaker with the main solution. When the solution is cool, add dilute nitric acid drop by drop until it has a faint acid reaction, and then add a little pure calcium carbonate to neutralize the excess of acid. Filter off the excess of calcium carbonate and wash the chlorides out of the filter with distilled water. To the filtrate, add a few drops of a cold saturated solution of potassium chromate, and then introduce a standard solution of silver nitrate from a burette, while stirring the solution constantly, until a permanent red color is imparted to it. From the amount of silver solution used to precipitate the chlorine, calculate the weight of sodium chloride in 10 cubic centimeters of the urine, and, from this result, calculate the percentage of sodium chloride, or the amount passed in 24 hours.

A standard solution of silver nitrate of almost any strength may be used for this determination, but, if many determinations are to be made, it is handy to have a solution of such strength that 1 cubic centimeter of it represents .01 gram of sodium chloride. This solution may be prepared by dissolving 29.06 grams of pure silver nitrate in distilled water and diluting the solution to 1 liter, but it is better to standardize it against a solution of sodium chloride, as described under Examination of Water.

QUANTITATIVE ANALYSIS

(PART 8)

ANALYSIS OF DAIRY PRODUCTS

NATURE AND COMPOSITION OF MILK

1. Milk consists of water, fat, proteids, sugar, and mineral matters. It is the nutritive secretion of nursing mammals, its secretion being the result of pregnancy and delivery at term, and continues for a variable period. The chemistry of its formation is not entirely understood, and as the organic ingredients of the milk do not exist in appreciable quantities in the blood, they must, therefore, be produced by a specific secretory action. It varies in composition according to the special peculiarities of the cow as to the breed, nature of the food, and period of lactation.

The average composition of 3,000 samples of milk compiled from analyses reported in the reports and bulletins of the agricultural experiment stations of the various states, gives approximately:

Water	87.50%
Total solids	12.50%
Fats	3.60%
Solids not fat	8.90%
Proteids	3.40%
Milk sugar	4.75%
Ash	.75%

The composition of the milk from different breeds, as given by the New York Experiment Station, for one year was:

Breeds	Total Solids Per Cent.	Fat Per Cent.	Proteids Per Cent.	Milk Sugar Per Cent.	Ash Per Cent.
Holstein-Friesian.......	12.39	3.46	3.39	4.84	.74
Ayrshire..............	13.06	3.57	3.43	5.33	.70
Jersey................	14.41	5.61	3.91	5.15	.74
American Holderness...	12.63	3.55	3.39	5.01	.70
Guernsey..............	14.60	5.12	3.61	5.11	.75
Devon	13.77	4.15	3.76	5.07	.76

It must be remembered that these figures are not necessarily true for all cases, because there is frequently as great a difference in the composition of milk from cows of the same breed as between cows of different breeds. The figures are therefore of value simply for the sake of illustration. The student should remember that in general the figures are: Solids, 12 to 13 per cent., occasionally as high as 15 per cent.; fat, 3 to 4 per cent., occasionally as high as 5 or 6 per cent.; proteids, 3.25 to 3.75 per cent.; sugar, 4.75 to 5.35 per cent.; ash, .75 per cent.—this is more constant than the other constituents.

The total yield of the various solids is of more importance than the percentage of composition. This is obtained by multiplying the percentages by the number of pounds of milk.

2. Fat occurs in milk in globules varying in size from .0015 millimeter to .005 millimeter in diameter; it consists of a mixture of the ethers of glyceryl C_3H_5, but is peculiar among other animal fats in containing a notable proportion of acid radicals with a small number of carbon atoms. Thus, about 91 per cent. consists of stearin, palmitin, and olein, and the remaining 9 per cent. of butyrin and caproin, along with minute amounts of caprin, myristin, and caprylin. The exact arrangement of the constituents is not known, but the

general opinion is that milk fat is not a mixture of simple fats, but that several acid radicals are united to the same glyceryl molecule.

3. Proteids.—It is generally accepted that the proteids in milk exist in at least three forms, *casein*, *albumin*, and *globulin*, the casein being present in by far the greater amount, and the globulin as traces only.

Casein is in a large part, at least, in a gelatinous form, probably in combination with calcium phosphate. It is precipitated from this condition by acids, rennet, magnesium sulphate, and other substances. Acids precipitate the casein by breaking up its combination with calcium phosphate. The action of rennet appears to be a more complex one, and is supposed to depend on the presence of calcium salts; thus, if the curd precipitated by dilute acids is dissolved in a dilute alkali solution and neutralized, it is unaffected by rennet, but regains its coagulability by the addition of a solution of a calcium salt, or, what amounts to the same thing, a little of the whey from which the casein was precipitated. It appears that rennet decomposes the casein into two proteids, one of which is precipitated in the curd. Some chemists use the term "caseinogen" to designate the form in which the casein exists when in solution or precipitated by acids, and reserve the term "casein" for the curd produced by rennet.

The *albumin* of milk appears to be a distinct form, and is generally known as *lactalbumin*. It is not precipitated by dilute acids, but is coagulated by heating to 70° to 75°. The proportion in cow's milk ranges from .35 to .50 per cent., although colostrum (see Art. **5**) may contain a much larger proportion. The composition of lactalbumin is usually given as:

Carbon	52.19%
Hydrogen	7.18%
Nitrogen	15.77%
Oxygen	23.13%
Sulphur	1.73%

Globulin occurs only in minute quantities in normal milk,

but colostrum may contain as much as 8 per cent. It coagulates on heating.

4. Lactose.—This is the sugar of milk and is peculiar to it; it has the composition $C_{12}H_{22}O_{11}$ and crystallizes with 1 molecule of water. In contact with yeast, lactose undergoes alcoholic fermentation, although with difficulty; it undergoes the lactic fermentation, however, very readily under the influence of certain microbes. When milk is evaporated rapidly to dryness, as in the determination of the total solid residue, the milk sugar is left in the anhydrous state.

5. Colostrum.—The term **colostrum** is applied to the milk secreted in the early stage of lactation. Usually, it has a marked difference from ordinary milk. It contains characteristic structures known as *colostrum corpuscles.* They are present for a variable period—3 to 14 days, but may persist even longer. Colostrum usually contains much less fat than fully developed milk, but a larger proportion of proteids, the increase being principally in the albumin and in the globulin. Colostrum is usually acid to litmus.

6. Normal milk is an opaque, white, or yellowish-white, fluid, nearly odorless, with a faintly sweet taste. Its opacity is due partly to the fat globules, although their removal does not render the milk transparent. The reaction of freshly drawn milk is amphoteric, that is, it turns blue litmus paper red, and red litmus paper blue. Its specific gravity varies between 1.028 and 1.035. It undergoes a gradual augmentation for a considerable time, but after about 5 hours, its specific gravity becomes stationary if kept at a temperature of 15°, although, at a higher temperature, it may require 24 hours to acquire constancy. This change is not dependent on the escape of gas, and is believed to be due to some molecular modification of the casein.

Unless collected with special care and under conditions of extreme cleanliness, milk always contains bacteria and animal

matter of an offensive character, such as blood, pus cells, etc. Many minute organisms, especially bacteria, propagate with great rapidity in milk and produce changes in its composition. Some specific organisms, such as the *Spirillum choleræ*, multiply to only a limited extent in ordinary milk, being hampered by other bacteria present, but, when introduced into sterilized milk, increase with great rapidity.

At ordinary temperature, milk soon undergoes decomposition under the influence of the microbes present, by which the milk sugar is converted principally into lactic acid, and the proteids are partly decomposed and partly coagulated. The liquid becomes sour and the fat is enclosed in a coagulated casein. In the initial state of decomposition, the proteids frequently undergo transformation into substances that are the cause of the violent poisonous effects occasionally produced by ice cream and other articles of food into the preparation of which milk enters.

ANALYTICAL PROCESSES

7. The determinations usually made are those of specific gravity, total solids, ash, fat, total proteids, casein, albumin, and sugar, to which the determinations of the amount of cream and opacity, which give some idea of the quality of the milk, may be added.

ARBITRARY METHODS

8. Opacity of Milk.—The opacity of the milk is doubtless due to the presence of the suspended fat particles and to the colloid casein. On the latter, it is probably principally dependent, since the color of the milk is not sensibly changed when practically all the fat is removed, as has been previously stated. Some idea of the quality of the milk, however, may be obtained by determining its opacity. This is accomplished by the use of a lactoscope. The one generally employed was devised by Feser, and is shown in Fig. 1.

This instrument consists of a cylindrical glass vessel of little more than 100 cubic centimeters capacity, in the lower part of which is set a cone of white glass marked with black lines. In this part are placed 4 cubic centimeters of milk. A small quantity of water is added and the contents of the vessel shaken. The addition of water is repeated until the black lines on the white glass just become visible. The graduations on the left side show the volume of water that has been added to bring the dark lines into view, while those on the right indicate, approximately, the percentage of fat present.

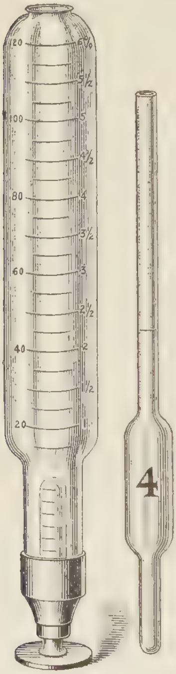


Fig. 1

9. Creamometer. The volume of cream that a sample of milk affords under arbitrary conditions of time and temperature is sometimes of value in judging the quality of milk. A convenient creamometer is a small cylinder graduated in such a way that the volume of cream separated in a given time can be easily noted. There are many kinds of apparatus used for this purpose, a typical one being shown in Fig. 2. The usual time for setting is 24 hours.

Fig. 2

SPECIFIC GRAVITY

10. The specific-gravity determination is to be made only after the spontaneous rise that is peculiar to milk has ceased. This will require about 5 hours after the milk is drawn, if it has been kept below 15°, but, at a

higher temperature, it will be necessary to allow at least 12 hours. The specific gravity of milk varies in general from 1.028 to 1.034. Nearly all good cow's milk will show a specific gravity varying from 1.030 to 1.032. In extreme cases from single cows, the limits may exceed those first given above, but such milk cannot be regarded as normal.

Increasing quantities of solids, not fat in solution, tends to increase the specific gravity, while an excess of fat tends to decrease it. There is a general ratio existing between the solids not fat and the fat in cow's milk, which may be expressed as 9 : 4. The removal of cream and the addition of water in such a manner as not to affect the specific gravity of the sample, disturbs this ratio. The determination of the specific gravity alone, therefore, cannot be relied on as an index of the purity of milk.

11. Lactometer.—A hydrometer especially constructed for use in the determination of the specific gravity of milk is called a **lactometer.** One of the most commonly used is known as the *lactometer of the New York Board of Health.* It is a hydrometer, delicately constructed, with a large cylindrical air space and a stem carrying the thermometric and lactometric scale, as is shown in Fig. 3. The milk is brought to a temperature of 15.5° and the reading of the lactometer scale observed. This is converted into a number expressing the specific gravity by means of a table of corresponding values accompanying each instrument and given in Table I. Each mark on the scale of the instrument corresponds to 2 degrees, and these marks extend from 0° to 120°.

FIG. 3

The minimum density for whole milk at $15\frac{1}{2}°$ is fixed by this instrument at 100°, corresponding to a specific gravity of 1.029. The mean density of many thousand samples of pure milk, as observed by the New York health authorities, is 1.0319.

TABLE I

TABLE SHOWING SPECIFIC GRAVITIES CORRESPONDING TO DEGREES OF THE NEW YORK BOARD OF HEALTH LACTOMETER. TEMPERATURE, 15.5° (60° F.)

Degrees	Specific Gravity	Degrees	Specific Gravity	Degrees	Specific Gravity
90	1.02619	101	1.02928	112	1.03248
91	1.02639	102	1.02958	113	1.03277
92	1.02668	103	1.02987	114	1.03306
93	1.02697	104	1.03016	115	1.03335
94	1.02726	105	1.03045	116	1.03364
95	1.02755	106	1.03074	117	1.03393
96	1.02784	107	1.03103	118	1.03422
97	1.02813	108	1.03132	119	1.03451
98	1.02842	109	1.03161	120	1.03480
99	1.02871	110	1.03190		
100	1.02900	111	1.03219		

TOTAL SOLIDS

12. The determination of the **total solids** meets with a number of difficulties, and many processes have been proposed. It is not possible here to describe all of them, but two of the most frequently used methods are here given.

13. The determination of total solids is made by evaporating, in a shallow flat dish of platinum 5 centimeters in diameter, an accurately weighed quantity of milk. The milk must be spread evenly in a thin layer, and should only cover the dish with a very thin film of milk. If the ash is also to be determined, about 5 grams should be accurately weighed in the dish, evaporated quickly to apparent dryness over the water bath, and the heating continued in the air bath at 100° C. until the weight becomes practically constant, which will require about 3 hours. If the evaporation is

carried on slowly, some decomposition occurs and the residue is brown, but if the larger portion of the water is evaporated quickly, a white residue is obtained. When the ash is not to be determined, it is recommended to use only 3 grams.

14. Babcock's Method.—When a higher degree of accuracy is required, the method of Babcock, which is adopted by the Association of Official Agricultural Chemists, should be employed. The method is conveniently carried on as follows: Provide a hollow cylinder of perforated sheet metal about 60 millimeters long and 20 millimeters in diameter, closed 5 millimeters from the bottom by a disk of the same material. The perforations should be about .7 millimeter in diameter, and as close together as possible. Fill loosely with from $1\frac{1}{2}$ to $2\frac{1}{2}$ grams of dry woolly asbestos and weigh. Introduce a weighed quantity of milk (about 5 grams). Dry at 100° for 4 hours. During the first part of the drying, the door of the oven should be partly left open to allow the escape of moisture. Cool in a desiccator and weigh; repeat drying until constant weight is obtained. The residue may be preserved for the determination of the fat.

15. Calculations of Total Solids.—As the density of a milk and the amount of fat in it can be quickly and accurately determined, many chemists prefer to calculate the total solids. Many arbitrary formulas have been proposed, and all of them may be used with satisfactory results, when the samples do not vary widely from the normal. A formula giving very satisfactory results, which vary less than .05 per cent. from the analytical results, is the formula worked out by Babcock:

$$t = \left(\frac{100\,S - FS}{100 - 1.0753\,FS} - 1\right)(250 - 2.5\,F) \qquad (1)$$

Where t = total solids not fat;
S = specific gravity of sample;
F = fat.

EXAMPLE.—Let the specific gravity S of a sample of milk be 1.03016 and the percentage of fat 3.33; what is the percentage of the total solids?

SOLUTION.—Substituting the known values, we obtain

$$t = \left[\frac{100 \times 1.03016 - (3.33 \times 1.03016)}{100 - (1.0753 \times 3.33 \times 1.03016)} - 1\right](250 - 2.5 \times 3.33)$$

$$t = \left(\frac{103.016 - 3.43043}{100 - 3.68874} - 1\right)(250 - 8.325)$$

$$t = (1.03399 - 1)(241.675)$$

$$t = .03399 \times 241.675 = 8.215$$

Then, total solids not fat = 8.215, and fat = 3.33; hence, total solids = 8.215 + 3.33 = 11.545%. Ans.

ASH

16. The residue from the determination of total solids is heated cautiously over the Bunsen burner, until a white ash is left. The results obtained in this manner are apt to be slightly low from loss of sodium chloride, etc.

17. Method of Association of Official Agricultural Chemists.—The method recommended by this association is as follows: In a weighed dish are placed 20 cubic centimeters of milk, to which 6 cubic centimeters of nitric acid are added; the whole is evaporated to dryness and ignited at a low, red heat until the ash is free from carbon.

FAT

18. A large number of fat-extraction methods have been worked out and proposed, and it is here only possible to describe a few of the simpler ones.

19. Paper-Coil Method.—This method, which is also known, from its originator, as **Adam's method,** consists essentially in spreading the milk over absorbent paper, drying, and extracting the fat in an extraction apparatus; the milk is distributed in a very thin layer, and by a selective action of the paper the larger portion of the fat is left on the surface. It is essential that the paper contains no materials

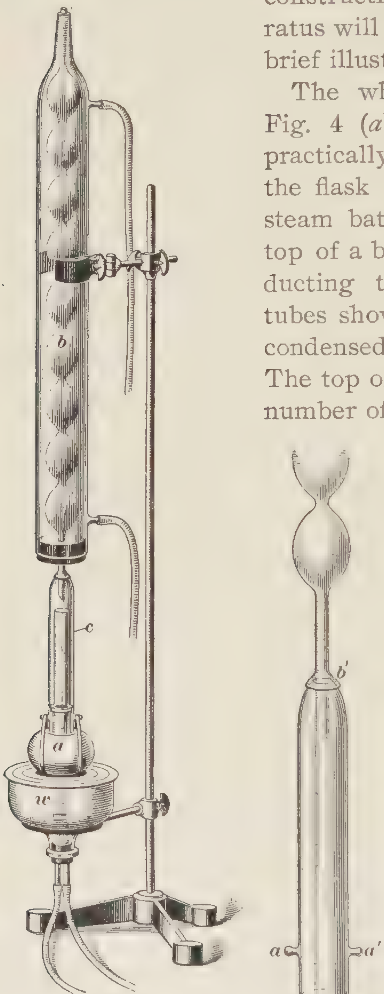
soluble in the liquid used for extraction. A paper, manufactured especially for this purpose by Schleicher and Schuell, is obtained in strips of suitable size.

The procedure is as follows: 5 cubic centimeters of the milk are discharged in a beaker 5 centimeters high and 3.5 centimeters in diameter. The charged beaker is weighed, and a strip of the paper, which has been rolled into a coil, thrust into it. In a few minutes, the paper will absorb nearly the whole of the milk. The coil is then carefully withdrawn, and stood, dry end downwards, on a watch glass. With a little practice, all but the last fraction of a drop will be absorbed by the paper. The beaker is again weighed and the weight of the milk taken is found by the difference. It is of importance to take up the whole of the milk from the beaker, as the paper has selective action, removing the watery constituents by preference over the fat. The charged paper is placed in the drying oven on a watch glass, milk end upwards, and dried. Usually an hour is sufficient. It is then inserted into the extraction tube of a Knorr continuous-extraction apparatus (see Fig. 4), the previously weighed flask *a* of which should have a capacity of about 150 cubic centimeters and contain about 75 cubic centimeters of anhydrous, alcohol-free ether, or petroleum spirit, boiling at about 45°. Heat is applied by means of the water bath. After the coil has received at least 10 to 12 washings, the flask is detached, the ether removed by distillation, and the fat dried by heating in an air oven at 105°. After cooling, the flask is wiped clean with a piece of silk, allowed to stand 10 minutes, and then weighed. Thimble-shaped cartridges made of fat-free paper are now made and are very convenient for holding the absorbent material on which the milk is spread; such a case may be used several times.

When the Babcock method (see Art. **14**) has been used, the cylinder and contents may be placed in the extraction tube and extracted as described.

20. Knorr's Continuous-Extraction Apparatus.—A large number of extraction apparatus have been constructed.

Knorr's extraction apparatus deserves preference, owing to its compactness, and the absence of stoppers, etc. The construction and operation of the apparatus will be readily understood by a brief illustrated description.



(a) (b)

FIG. 4

The whole apparatus is shown in Fig. 4 (*a*), and it is seen that it is practically an upright condenser. *a* is the flask containing the solvent, *w* a steam bath made by cutting off the top of a bottle, inverting it, and conducting the steam into one of the tubes shown in the stopper, while the condensed water runs out of the other. The top of the bath is covered with a number of concentric copper rings, so that the opening may be made of any desirable size. *b* represents the condenser, which is a long glass tube, on which a number of bulbs have been blown, and which is attached to the hood *c* for holding the material to be extracted, as represented in Fig. 4 (*b*) at *b*′, making a solid glass union. Before joining the tube at *b*′, the rubber stopper, which is to hold it to the outside condenser of *b*, is slipped on.

A more detailed description of the different parts of the apparatus can be seen from consulting Figs. 5 and 6. In (*a*), Fig. 5, is represented a section of the flask that holds the solvent,

showing how the sides of the hood containing the material to be extracted pass over the neck of the flask. A view of the flask itself is shown in (*b*), Fig. 5. It is made by taking an ordinary flask, softening it about the neck and pressing the neck in so as to form a cup, as indicated in (*a*), to hold the mercury, which forms the union of the flask with the condenser. The flask is held in position by passing a rubber band below it, which is

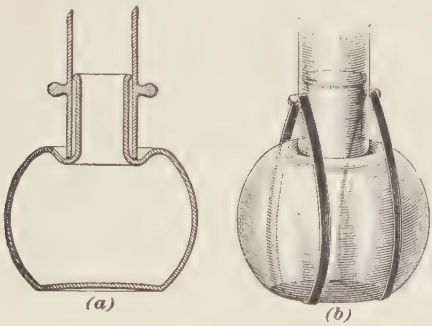


FIG. 5

FIG. 6

attached to the two glass nipples *a*, *a′*, shown in (*b*), Fig. 4. The material to be extracted may be contained in an ordinary tube, as shown in Fig. 6, which may be made from a test tube drawn out, as indicated in the illustration, having a perforated platinum disk sealed in at *a*. The containing tube rests on the edges of the flask containing the solvent, by means of nipples shown at *b*, *b′*.

21. Werner-Schmidt Method.—A very satisfactory and simple method for the determination of fat is that originated by Werner and Schmidt and recommended by Dr. Leffmann. It is especially suitable for sour milk.

Into a long test tube of 50 cubic centimeters capacity, graduated to tenths of cubic centimeters, 10 cubic centimeters of milk are measured and 10 cubic centimeters of strong hydrochloric acid added, or the milk may be weighed in a small beaker and washed into the tube with the acid. After mixing, the liquid is boiled $1\frac{1}{2}$ minutes, or the tube may be

corked and heated in the water bath from 5 to 10 minutes, until the liquid turns brown; but it must *not* be allowed to turn black. The tube and its contents are cooled in water, 30 cubic centimeters of ether are then added, the whole shaken, and allowed to stand until the line of acid and ether is distinct. The cork is taken out and a double tube arrangement, as shown in Fig. 7, inserted. The stopper of this should be of cork, since it is rather difficult to slide the glass tube in a rubber one, and to avoid the possibility of the ether acting upon the rubber. The lower end of the exit tube *b* is adjusted so as to rest immediately above the junction of the two liquids. By blowing into *a*, the ethereal solution is blown out and received in a weighed flask. Two more portions of ether, 10 cubic centimeters each, are shaken with the acid liquid, blown out again, and added to the first. The ether is then distilled off and the fat dried and weighed.

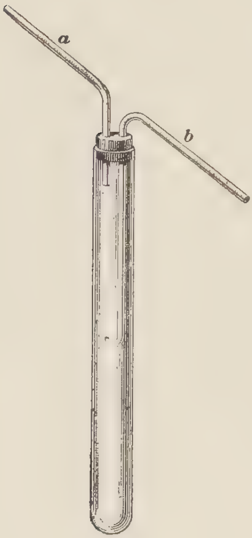
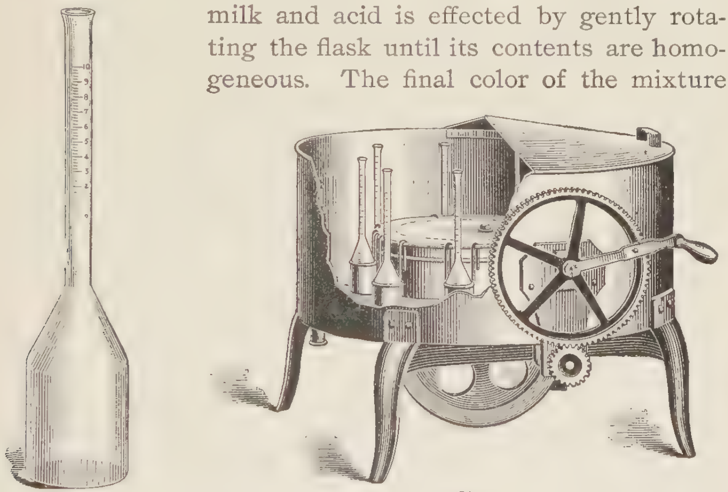


FIG. 7

22. Babcock's Method.—Among the many quick volumetric methods that have been proposed for the determination of fat in milk, none has secured so wide an application as that suggested by Babcock.

The chief point of advantage in the use of this method is found in effecting the solution of the casein by means of sulphuric acid of about 1.83 Sp. Gr. By this reagent, the casein is dissolved in a few moments without the aid of any other heat than that generated by mixing the milk with the reagent. The bottle in which the separation is made is shown in (*a*), Fig. 8. The graduations on the neck are based on the use of 18 grams of milk. To avoid the trouble of weighing, the milk is measured from a pipette graduated

to deliver 18 grams of milk of the usual specific gravity. While it is true that normal milk may vary somewhat in its density, it has been found that a pipette marked 17.6 cubic centimeters delivers a weight that can be safely assumed to vary but slightly from the one desired. The graduated bottle holds easily 35 cubic centimeters in its expanded portion, and the volume of milk just noted is mixed with an equal volume of sulphuric acid. The complete mixture of the milk and acid is effected by gently rotating the flask until its contents are homogeneous. The final color of the mixture varies from brown to black. While still hot, the bottles are placed in a centrifugal machine shown in (*b*), Fig. 8, and the whole whirled for at least 5 minutes. The revolutions should be at least between 700 and 1,000 per minute. After the expiration of 5 minutes, the bottles are taken out of the centrifuge and filled to the upper mark with hot water, replaced in the machine, and whirled again for 2 minutes. The fat will then be found in a clearly defined column in the graduated neck of the bottle. In reading the scale, the extreme limits between the lowest point marked by the lower meniscus and the highest point marked by the edge of the upper meniscus are to be regarded as the termini of the fat column.



(*a*) (*b*)

FIG. 8

TOTAL PROTEIDS

23. Estimation of Total Proteid Matter.—This determination is most conveniently made by calculation from the figure for total nitrogen obtained by Gunning's modification of Kjeldahl's process. The reagents and apparatus required are as follows:

1. $\frac{n}{10}$ *sulphuric acid.*

2. $\frac{n}{10}$ *ammonia solution.*

3. *Acid Potassium-Sulphate Solution.*—This solution is made by heating two parts of strictly chemically pure sulphuric acid with one part of chemically pure potassium sulphate, until the latter is entirely dissolved. The mixture is in a semisolid state, when cold, but may easily be liquefied by warming gently.

4. *A saturated solution of sodium hydrate.*

5. *Digestion and Distillation Flask.*—A flask should be chosen that has a capacity of about 600 cubic centimeters, and cylindrical neck about 18 centimeters long and 2.5 centimeters in diameter. It is supported on wire gauze and the mouth covered by inserting a funnel during the digestion. For distilling, a well fitting rubber stopper with delivery tube should be attached. The tube should be of the same diameter as the condensing tube, and should have one or two bulbs, about 4 centimeters in diameter, to prevent any solution being carried over by spurting. It should project slightly below the stopper and be cut obliquely.

6. *Condenser.*—The condensing tube should be of block tin, and have an external diameter of about 1 centimeter. At least 30 centimeters of its length should be in contact with the cooling water. The junction of the glass and tin tube is made by a short, close fitting rubber tube, and the tubes are so bent as to slope forwards toward the distilling flask. The lower end of the tin tube is connected by a short rubber tube with a glass bulb tube that dips below the surface of a measured volume (20 cubic centimeters) of the

standard sulphuric acid in an Erlemeyer flask of about 300 cubic centimeters capacity.

24. Five cubic centimeters of the milk are weighed or measured into the flask and evaporated to dryness over the water bath; 30 cubic centimeters of the acid potassium-sulphate mixture are added and heated over the Bunsen burner. At first, frothing occurs and white fumes escape, consisting chiefly of water vapor. To prevent loss of acid, the neck of the flask is fitted with a funnel that is covered with a watch glass. This will cause the acid to condense and run back into the flask. The operation is finished when the liquid is colorless, and generally requires about an hour. After it has cooled, about 200 cubic centimeters of distilled water and sufficient of the sodium-hydrate solution are added to make the mixture strongly alkaline. Forty to 50 cubic centimeters of the sodium-hydrate solution will be, as a rule, required for this purpose. It should be poured down the sides of the flask so that it does not mix at once with the acid. The flask is now connected with the condenser, and the contents mixed by shaking. The liquid is then distilled until the whole of the ammonium hydrate is collected, which will usually be the case when about 150 cubic centimeters have passed over. The receiver and short tube dipping in it are then detached, and the distillate titrated to determine the amount of acid neutralized. From this, the amount of ammonium hydrate is calculated, and the nitrogen in this multiplied by 6.38 will give the figure for the total proteids.

The Association of Official Agricultural Chemists recommends an indicator prepared as follows: 3 grams of cochineal are digested for several days in a mixture of 50 cubic centimeters of strong alcohol and 200 cubic centimeters of water. After being filtered, the solution is ready for use.

25. Determination of Total Proteids by Copper Sulphate.—This method, which is due to Ritthausen, depends on precipitation by copper sulphate and sodium hydrate. The reagents required are as follows:

1. *Copper Sulphate Solution.*—Pure crystallized copper sulphate, to the amount of 34.639 grams, is dissolved in distilled water, and the solution made up to 500 cubic centimeters.

2. *Sodium Hydrate Solution.*—A suitable solution is prepared by dissolving 12 grams of $NaOH$ in 500 cubic centimeters of water.

Ten grams of the milk are placed in a beaker, diluted with 100 cubic centimeters of distilled water, 5 cubic centimeters of the copper-sulphate solution added by means of a pipette, and the whole thoroughly mixed. While constantly stirring, the sodium-hydrate solution is then carefully added drop by drop, until the precipitate settles quickly and the solution becomes neutral. Great care should be exercised to avoid any excess of the alkali, as an excess prevents the complete precipitation of the proteids. When the operation is correctly performed, which requires little practice, the precipitate, which includes the fat, settles quickly, and carries down all the copper. The mixture is poured into a filter, previously dried at 130°, and weighed; the precipitate is washed with hot water, first by decantation, and then on the filter. The filtrate and washing are set aside for the determination of sugar, as described later, and the precipitate washed with alcohol to remove all traces of water, and dried. The fat is then removed from the dry precipitate by extraction with ether, as has been previously described; the residue is dried and weighed, then transferred to a porcelain crucible, incinerated, and again weighed. The weight of the filter and contents, less that of the filter and residue after ignition, gives the weight of the proteids. The results are slightly high.

CASEIN AND ALBUMIN

26. Official Method for Determination of Casein. The determination of casein in milk should be made when the milk is fresh, or, at least, nearly so. If it is not possible to make this determination within the first 24 hours after the milking, 1 part of formaldehyde should be added to every 2,500 parts of milk, and the whole kept in a cool place.

Ten grams of milk are placed in a beaker, and 90 cubic centimeters of water, having a temperature of 40° to 42°, are added. To this, 1.5 cubic centimeters of a solution containing 10 per cent., by weight, of acetic acid are added, the whole stirred with a glass rod and then allowed to stand from 3 to 5 minutes. The supernatant liquid is then decanted through the filter, the precipitate washed 2 or 3 times by decantation with a moderate quantity of cold water, and finally transferred to the filter, and washed on the filter twice. The filtrate should be clear, or nearly so. Should it not be clear when it first runs through, it can generally be made so by two or three repeated filtrations, after which the washing of the precipitate can be completed.

The washed precipitate and filter are transferred to the flask used in Gunning's modification of Kjeldahl's method for the determination of nitrogen, and the nitrogen determined as explained in Art. **23.** The nitrogen thus obtained, multiplied by 6.38, gives the amount of casein in the sample.

In working with milk that has been kept with a preservative, the acetic acid should be added in small proportions, a few drops at a time, while stirring, and the addition continued until the liquid above the precipitate becomes clear, or very nearly so.

27. Official Method for the Determination of Albumin.—The filtrate obtained in the determination of casein is neutralized with caustic alkali, $\frac{3}{10}$ cubic centimeter of a 10-per-cent. solution of acetic acid added, and the mixture heated to the temperature of boiling water for from 10 to 15 minutes. The precipitate is collected on a filter, washed 2 or 3 times with cold water, and the nitrogen determined therein in exactly the same way as indicated in Art. **24.** The nitrogen thus obtained, multiplied by 6.38, gives the amount of albumin present in the sample.

28. Remaining Nitrogen Compounds.—The remaining compound or compounds of nitrogen are determined by difference, subtracting from the amount of total nitrogen compounds the sum of the casein and albumin.

SUGAR

29. Soxhlet's Method.—The following method, due to Soxhlet, employs a Fehling's solution, made as required, by mixing equal parts of the following solutions:

Copper-Sulphate Solution.—Pure crystallized copper sulphate, to the amount of 34.639 grams, is dissolved in distilled water and made up to 500 cubic centimeters.

Alkaline-Tartrate Solution.—Pure sodium-potassium tartrate, equal to 173 grams, and 51 grams of pure sodium hydrate are dissolved and the solution made up to 500 cubic centimeters.

Of the mixed filtrate obtained in the determination of total proteids by Ritthausen's method (see Art. **25**), 100 cubic centimeters are boiled, and 50 cubic centimeters of boiling Fehling's solution added, and the boiling of the mixture continued for exactly 6 minutes. The precipitate is allowed to settle, and the heating continued for 2 minutes, after which the precipitate is brought on a filter, washed three times with boiling water, twice with alcohol, and finally with ether. The filter and precipitate are then dried, the latter removed to a watch glass, and the filter burned in a porcelain crucible, whose weight has been previously ascertained. The precipitate is added, and the cuprous oxide converted into cupric oxide by strong ignition over a Bunsen burner for about 10 minutes.

The amount of copper reduced under these conditions is not directly porportional to the milk sugar present. Table II shows the amount of milk sugar $C_{12}H_{22}O_{11} \cdot H_2O$ equivalent to the given weights of copper. The volumes of Fehling's solution and sugar solution must conform strictly to the figures here given.

The figures given in Table II are the weights of copper and lactose. The equivalent weights of copper and cupric oxide are almost exactly in the ratio of 4 to 5; hence, to obtain the weight of copper from that of cupric oxide in the above determination, we need only multiply the weight of cupric oxide by .8.

For the amounts of copper intermediate between those given in the table, the quantity of lactose is determined by the factor in the third column, which represents the weight of copper corresponding to 1 milligram of lactose at that point. If, for instance, 178 milligrams of copper are obtained, the calculation will be as follows:

$$\begin{aligned} 175 \text{ milligrams } Cu &= 127.80 \\ 3 \text{ milligrams } Cu \times .75 &= \underline{\quad 2.25} \\ 178 \text{ milligrams } Cu &= 130.05 \text{ mg. } C_{12}H_{22}O_{11} \cdot H_2O \end{aligned}$$

TABLE II

WEIN'S TABLE FOR EQUIVALENT WEIGHTS OF LACTOSE, CALCULATED FOR USE IN SOXHLET'S METHOD

Copper	Lactose	Factor	Copper	Lactose	Factor	Copper	Lactose	Factor
120	86.4	.73	215	158.2	.76	310	232.2	.81
125	90.1	.73	220	161.9	.76	315	236.1	.81
130	93.8	.74	225	165.7	.76	320	240.0	.81
135	97.6	.74	230	169.4	.76	325	243.9	.81
140	101.3	.74	235	173.1	.76	330	247.7	.82
145	105.1	.74	240	176.9	.76	335	251.6	.82
150	108.8	.74	245	180.8	.77	340	255.7	.82
155	112.6	.75	250	184.8	.77	345	259.8	.82
160	116.4	.75	255	188.7	.78	350	263.9	.82
165	120.2	.75	260	192.5	.78	355	268.0	.82
170	123.9	.75	265	196.4	.78	360	272.1	.82
175	127.8	.75	270	200.3	.79	365	276.2	.82
180	131.6	.75	275	204.3	.80	370	280.5	.85
185	135.4	.76	280	208.3	.80	375	284.8	.85
190	139.3	.76	285	212.3	.80	380	289.1	.85
195	143.1	.76	290	216.3	.80	385	293.4	.85
200	146.9	.76	295	220.3	.80	390	297.7	.85
205	150.7	.76	300	224.4	.81	395	302.0	.85
210	154.5	.76	305	228.3	.81	400	306.3	.85

ANALYSIS OF BUTTER

PRELIMINARY REMARKS

30. Butter, a mixture of fat, water, and curd, is obtained by churning cream from cow's milk. The water contains, in solution, milk sugar and the salts of milk. Common salt is usually present, being added after the churning, and artificial coloring is frequently used.

The composition of butter usually varies within the following limits: Fat, 78 to 94 per cent.; curd, 1 to 3 per cent.; water, 5 to 14 per cent.; and salt, 0 to 7 per cent.

31. Nostrums for Butter Making.—Preparations are sold purporting to possess the property of increasing the yield of butter from a given quantity of milk. These preparations are simply made up to deceive, and mostly contain rennet or pepsin, salt, and very often annatto. These ingredients curdle the milk, and allow the incorporation of much cheese and water with the butter, hence the increased yield, at the expense of the quality of the butter.

Samples of butter have thus been met that contained as much as 40 per cent. of water, while it is generally considered that the maximum amount of water should not exceed 16 per cent. Butter containing an excess of water quickly turns rancid, and has a spongy and, unless artificially colored, pale appearance.

32. Sampling of Butter.—If large quantities of butter are to be sampled, a butter trier, or sampler, may be used. The portions thus drawn, about 500 grams, are to be perfectly melted in a closed vessel at as low a temperature as possible, and when melted the whole is to be shaken violently for some minutes until the mass is homogeneous, and sufficiently solidified to prevent the separation of the fat and water. A portion is then poured out into the vessel from which it is to be weighed for analysis, and should nearly or quite fill it. The sample should be kept in a cold place until analyzed.

ANALYTICAL PROCESSES

33. The following methods for the analysis of butter have been adopted by the Association of Official Agricultural Chemists:

34. Determination of Water.—From 1.5 to 2.5 grams of butter are dried to constant weight at the temperature of boiling water in a flat-bottomed glass dish, having a surface of at least 20 square centimeters. The use of clean, dry sand or asbestos with the butter is admissible, and is necessary if a dish with round bottom should be employed.

35. Determination of Fat.—The dry butter from the above water determination is dissolved in the dish with absolute ether, or with 76° petroleum spirit. The contents of the dish are then transferred to a Gooch crucible with the aid of a wash bottle filled with the solvent, and are washed until free from fat. The crucible and contents are heated at the temperature of boiling water until the weight is constant. The weight of fat is represented by the loss of weight of the dried butter.

36. Determination of Casein and Ash.—The Gooch crucible containing the residue from the fat determination, consisting of casein and salts, is covered and heated, gently at first, gradually raising the temperature to just below redness. The cover may then be removed and the heat continued until the contents of the crucible assumes a white color. The loss in weight of the crucible and contents represents the weight of the casein, and the residue in the crucible, ash, or mineral matter.

37. Determination of Salt.—It is the usual custom in the manufacture of butter in this country, to add, as a condiment, a certain proportion of salt. A convenient method of determining the quantity of salt is found in the removal thereof, from the sample, by repeated washing with hot water, and determining the salt in the wash water by titration with silver nitrate. The operation is conducted as follows:

From 5 to 10 grams of the sample are placed in a separatory funnel, hot water added, the stopper inserted, and the contents of the funnel well shaken. After standing until the fat has all collected on top of the water, the stop-cock is opened and the water is allowed to run into an Erlemeyer flask, being careful to let none of the fat globules pass. Hot water is again added to the sample, and the extraction is repeated several times, using each time from 10 to 20 cubic centimeters of water. The resulting washings contain all but a mere trace of the sodium chloride originally present in the butter. The sodium chloride is determined in the filtrate volumetrically by means of $\frac{n}{10}$ silver nitrate, using potassium chromate as an indicator.

SUBSTITUTES AND ADULTERANTS OF BUTTER

38. In this country, butter is never adulterated with cocoa or sesame oil, as is sometimes the case in European countries. The common substitute for butter here is oleomargarine, and the most common butter adulterant, neutral lard. The term *oleomargarine* includes now, by Act of Congress, any oleaginous substance intended as a substitute for butter, containing any proportion of fat other than butter fat. The principal materials employed in the preparation of butter substitutes are cottonseed oil, beef fat, and mutton fat.

39. When fats are saponified, and the soap treated with acid, the individual fatty acids are obtained. It is upon the recognition of the peculiar acid radicals existing in butter that the most satisfactory method of distinguishing it from other fats is based. Since the relative proportion of the radicals differs in different samples, the quantitative estimation cannot be made with accuracy, but when the foreign fats are substituted to the extent of 25 per cent. or more, the adulteration can be detected with certainty and an approximate quantitative determination made.

DETERMINATION OF VOLATILE ACIDS

40. Leffmann and Beam's Distillation Method. The fatty acids containing a small number of carbon atoms, set free by the process noted above, are soluble in water and volatile. A method for their estimation, depending on their solubility in water, was perfected by Hehner, but has now been displaced by a distillation method originally suggested by Hehner and Angell, but improved by Reichert and Wollny, and modified by Leffmann and Beam.

For this method, the following reagents are required:

Glycerol Soda.—Pure sodium hydrate, to the amount of 100 grams, is dissolved in 100 cubic centimeters of water, and allowed to stand until clear. Of this solution, 20 cubic centimeters are mixed with 180 cubic centimeters of pure concentrated glycerol.

Sulphuric Acid.—This reagent consists of 200 cubic centimeters of chemically pure concentrate sulphuric acid, made up with distilled water to 1 liter.

Barium Hydrate.—This reagent consists of an accurately standardized $\frac{n}{10}$ barium-hydrate solution.

Indicator.—An alcoholic solution of phenol phthalein is used as an indicator.

About 50 grams of butter are placed in a beaker, and heated to a temperature of 50° to 60°, until the water and the curd have settled to the bottom. The clear fat is then poured on a warm, dry, plaited filter, and kept in a warm place until 25 or 30 cubic centimeters have been collected. If the filtrate is not perfectly clear, it should be reheated for a short time and again filtered.

A 300-cubic-centimeter flask is washed thoroughly, rinsed with alcohol, and then with ether, and thoroughly dried by heating in the drying oven. After cooling, it is allowed to stand for about 15 minutes, and weighed.

A pipette, graduated to 5.75 cubic centimeters, is heated to about 60°, and filled to the mark with the well mixed fat, which is then run into the flask. After standing for about 15 minutes, the flask and contents are weighed; 20 cubic

centimeters of the glycerol soda are added, and the flask heated over the Bunsen burner. The mixture will foam more or less, but this may be controlled, and the operation accelerated, by shaking the flask. When all the water has been driven off, the liquid will cease to boil, and if the heat and agitation be continued for a few moments, complete saponification will be effected, the mixture becoming perfectly clear. The whole operation, exclusive of weighing the fat, requires less than 5 minutes. The flask is then withdrawn from the heat and the soap dissolved in 135 cubic centimeters of water. The first portion of water should be added drop by drop, and the flask shaken between each addition in order to avoid foaming. When the soap is dissolved, 5 cubic centimeters of the dilute sulphuric acid are added, a piece of pumice stone dropped in, and the liquid distilled until 110 cubic centimeters have been collected in a flask that is accurately graduated to that volume.

The arrangement of the apparatus for the distillation is shown in Fig. 9, and needs no further explanation. The

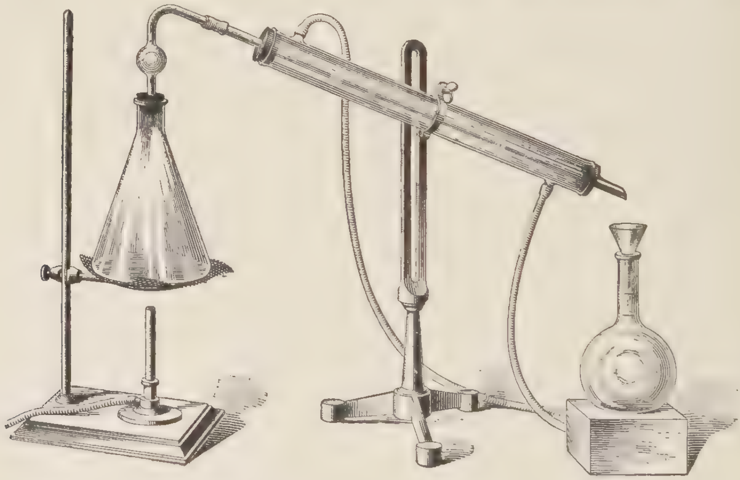


FIG. 9

flame should be so regulated that the above mentioned volume is collected within 30 minutes.

The 110 cubic centimeters of distillate, after thorough mixing, are filtered through a perfectly dry filter; 100 cubic centimeters of the filtered distillate are poured into a beaker having a capacity of from 200 to 250 cubic centimeters, .5 cubic centimeter of phenol-phthalein solution added, and decinormal barium hydrate run in until a red color is just produced. The contents of the beaker are then returned to the measuring flask, to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red color produced remains permanent for 2 or 3 minutes.

A blank experiment should be made to determine the amount of decinormal alkali required by the reagents required. With a good quality of glycerol, this will rarely exceed .5 cubic centimeter.

As a rule, 5 grams of butter yield a distillate that requires from 24 to 34 cubic centimeters of decinormal alkali solution, although several instances have been published in which genuine butter has given a figure as low as 22.5 cubic centimeters; such results are, however, very exceptional. The materials employed in the preparation of oleomargarine yield a distillate requiring usually less than 1 cubic centimeter of the decinormal barium-hydrate solution for neutralization. Commercial oleomargarine is, however, usually churned with milk, in order to secure a genuine butter flavor, and consequently acquires a small amount of butter fat; hence, the distillate of commercial oleomargarine usually requires from 1 to 2 cubic centimeters of barium-hydrate solution.

41. Method of Association of Official Agricultural Chemists.—For the method of determining the volatile acids, adopted by the Association of Official Agricultural Chemists, the following reagents are required:

Sodium-Hydrate Solution.—Chemically pure sodium hydrate, to the amount of 100 grams, is dissolved in 100 cubic centimeters of water. The sodium hydrate should be as free as possible from carbonates, and be preserved out of contact with the air.

Alcohol.—This reagent consists of alcohol of about 95 per cent. strength, redistilled with caustic soda.

Acid.—This reagent is a solution of sulphuric acid containing 200 cubic centimeters of strongest sulphuric acid in 1,000 cubic centimeters of water.

Barium-Hydrate Solution.—This reagent consists of an accurately standardized, approximately decinormal, solution of barium hydrate.

Indicator.—The indicator is a solution of 1 gram of phenolphthalein in 100 cubic centimeters of alcohol.

Saponification Flask.—This flask is made of hard, well annealed glass, capable of resisting the tension of alcohol vapor at 100°, and having a capacity of from 250 to 300 cubic centimeters.

Pipettes.—One pipette graduated to deliver 40 cubic centimeters, and another to deliver 5.75 cubic centimeters.

Distilling Apparatus.—An apparatus similar to that shown in Fig. 31.

Burette.—An accurately calibrated burette reading to tenths of a cubic centimeter.

The method of determining is as follows: The butter or fat to be examined should be melted, and kept in a dry, warm place at about 60° for 2 or 3 hours, until the water and curd have entirely settled out. The clear supernatant fat is poured off and filtered through dry filter paper, in a jacketed funnel containing hot water, as shown in Fig. 10. Should the filtered fat, in a fused state, not be perfectly clear, it must be filtered a second time.

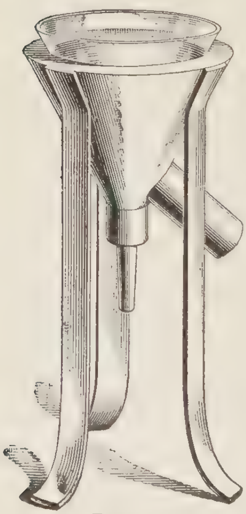


FIG. 10

The saponification flasks are prepared by having them thoroughly washed with water, alcohol, and ether, wiped perfectly dry on the outside, and heated for 1 hour at the temperature of boiling water. The flasks

should then be placed on a tray by the side of the balance, and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within 15 or 20 minutes of the time they are weighed. The weight of the flask having been accurately determined, they are charged with the fat in the following way:

A pipette, with long stem, marked to deliver 5.75 cubic centimeters, is warmed to a temperature of about 50°. The fat having been poured back and forth once or twice into a dry beaker, in order to thoroughly mix it, is taken up in the pipette and the nozzle of the pipette carried to near the bottom of the flask, having been previously wiped to remove any adhering fat, and 5.75 cubic centimeters of fat allowed to flow into the flask. After the flask has thus been charged, it should be recovered with a silk handkerchief and allowed to stand 15 or 20 minutes, when it is again weighed.

Then, 10 cubic centimeters of 95-per-cent. alcohol are added to the fat in the flask, and 2 cubic centimeters of the sodium-hydrate solution; a soft cork stopper is now inserted in the flask and tied down with a piece of twine. The saponification is then completed by placing the flask upon the water or steam bath. The flask during saponification, which should last 1 hour, should be gently rotated from time to time, being careful not to project the soap for any distance upon its sides. At the end of 1 hour the flask, after having been cooled to near the temperature of the room, is opened. The stopper having been laid loosely in the mouth of the flask, the alcohol is removed by dipping the flask into the steam bath. The steam should cover the whole of the flask except the neck. After the alcohol is nearly removed, frothing may be noticed in the soap, and to avoid any loss from this cause, or any creeping of the soap up the sides of the flask, it should be removed from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapor may be removed from the flask by waving it briskly, mouth down, to and fro. After the removal of the alcohol, the soap should be dissolved by adding 135 cubic centimeters

of recently boiled distilled water, warming on the steam bath with occasional shaking, until solution of the soap is complete. When the soap solution has cooled to about 65°, the fatty acids are separated by adding 5 cubic centimeters of the dilute sulphuric-acid solution mentioned previously. The flask should now be restoppered as in the first instance, and the fatty-acid emulsion melted by replacing the flask on the steam bath. According to the nature of the fat under examination, the time required for the fusion of the fatty-acid emulsion may vary from a few minutes to several hours.

After the fatty acids are completely melted, which can be determined by their forming a transparent, oily layer on the surface of the water, the flask is cooled to the temperature of the room, and a few pieces of pumice stone added. The pumice stone is prepared by throwing it, at a white heat, into distilled water, and keeping it under water until used. The flask is now connected with a glass condenser, slowly heated with a naked flame, until ebullition begins, and then the distillation continued by regulating the flame in such a way as to collect 110 cubic centimeters of the distillate in, as nearly as possible, 30 minutes. The distillate should be received in a flask accurately graduated at 110 cubic centimeters.

The 110 cubic centimeters of the distillate, after thorough mixing, are filtered through a dry filter paper and collected in a flask marked at 100 cubic centimeters. These 100 cubic centimeters of the filtered distillate are poured into a beaker holding from 200 to 250 cubic centimeters, .5 cubic centimeter of the phenol-phthalein solution added, and decinormal barium-hydrate solution run in until a red color is produced. The contents of the beaker are then returned to the 100-cubic-centimeter measuring flask, to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red color produced remains apparently unchanged for 2 or 3 minutes. The number of cubic centimeters of decinormal barium hydrate required should be increased by one-tenth.

DETECTION OF BUTTER ADULTERATION BY ACETIC ACID

42. Many other methods of detecting butter adulteration have been proposed; the distinction between butter and its adulterants is, however, not so distinct in the various methods proposed as it is in the distillation method described in the preceding articles. It is not possible to give all of these methods, and the student must refer to a book on agricultural chemistry, if he wishes information on this point. Only one, known as *Valenta's test*, will here be given.

43. Valenta's Test.—This simple test depends on the behavior of butter and acetic acid, and is the one of most value. The strength of the acetic acid may vary, but it must always be standardized against a sample of pure butter fat.

In a dry test tube are placed 3 cubic centimeters of the melted fat, and an equal volume of acetic acid added, and the mixture heated until solution has taken place. It is then allowed to cool spontaneously, and the temperature noted at which the liquid begins to get turbid.

After a large number of experiments, it has been found that an acetic-acid solution of 95.5 per cent. is the most efficient.

With an acid of such a strength, the following figures have been obtained:

Butter fat (24 samples)	
Highest	39°
Lowest	29°
Mean	36°
Oleomargarine (5 samples)	
Highest	97°
Lowest	94°
Mean	95°

Cottonseed oil, various samples	71°, 75°, 71°, 85°, 86°, 88°, 89°
Peanut oil	72°, 73°
Lard oil	75°, 76°, 75°
Lard	98°, 97°, 98°, 97°
Beef stearin	100°
Lard stearin	100°

Attention should be called to the fact that the presence of moisture in the fat is one of the most fruitful sources of error, and that it is generally recommended to filter the sample through dry filter paper before mixing with the acetic acid.

BUTTER COLORS AND THEIR DETECTION

44. Where cows are deprived of green food and root crops, such as carrots, and kept on poorly balanced rations, the butter made from their milk may be almost colorless. To remedy this defect, it is quite common practice to color the product artificially. Almost the sole coloring matter used in this country is annatto. Other coloring matters that are occasionally employed are turmeric, saffron, marigold leaves, yellow wood (*Chlorophora tinctoria*), carrot juice, chrome yellow (lead chromate), and dinitrocresol.

The use of small quantities of turmeric or saffron is unobjectionable from a sanitary point; that of annatto, to say the least, is offensive to the esthetic sense, stale urine being employed in its manufacture, while such a coloring substance as lead chromate is certainly dangerous to the health.

The detection of annatto or saffron in butter may be accomplished by the method of *Cornwall.*

45. Cornwall's Method for the Detection of Annatto and Saffron in Butter.—About 5 grams of warm and filtered fat are dissolved in about 50 cubic centimeters of ordinary ether, in a wide tube, and the solution vigorously shaken from 10 to 15 seconds, with from 12 to 15 cubic centimeters of a very dilute solution of caustic potash or soda in water, only alkaline enough to give a distinct reaction with turmeric paper, and to remain alkaline after separating from the ethereal fat solution. The corked tube is set aside, and in a few hours, at most, the greater part of the aqueous solution, now colored more or less yellow by the annatto, can be drawn from beneath the ether with a pipette in a sufficiently clear state to be evaporated to dryness, and tested with a drop of concentrated sulphuric acid.

Sometimes it is well to further purify the aqueous solution by shaking it with some fresh ether before evaporating it, and any fat globules that may float on its surface during evaporation should be removed by touching them with a slip of filter paper; but the solution should *not* be filtered, because the filter paper may retain much of the coloring matter.

The dry yellow or, perhaps, slightly orange residue turns, in the presence of annatto, blue or violet-blue with sulphuric acid, then quickly green, and finally brownish or somewhat violet, this final change being variable, according to the purity of the extract.

Saffron can be extracted in the same way; it differs from annatto very decidedly, the most important difference being the absence of the green coloration.

Genuine butter, free from foreign coloring matter, imparts at most a very pale-yellow color to the alkaline solution; but it is important to note that a mere green coloration of the dry residue, on addition of sulphuric acid, is not a certain indication of annatto, because the writer has thus obtained from genuine butter, free from foreign coloring matter, a dirty green coloration, but *not* preceded by any blue or violet tint.

46. Turmeric is easily identified by the brownish to reddish stratum that forms between the ethereal fat solution and the alkaline solution before they are intimately mixed. It may be even better recognized by carefully bringing a feeble alkaline solution of ammonia in alcohol beneath the ethereal fat solution with a pipette, and gently agitating the two, so as to mix them partially.

EXAMINATION OF FERTILIZERS

PRELIMINARY REMARKS

47. Fertilizers are manufactured by the mixing of various forms of refuse materials from other industries, where such material contain either nitrogen or phosphoric acid, or both, such as sugar scums, refuse from slaughter houses, fat melting, glue making, tanning, etc. The

principal source of phosphoric acid is the phosphate rock from the southern states, which, in the pulverulent form, is treated with sulphuric acid to render most of the phosphoric acid available, chiefly in the form of calcium superphosphate, and is then mixed in suitable proportions with materials more or less rich in nitrogen. Inevitably, the finished fertilizers in the market contain more or less of what is called "reduced," "inverted," or "reverted" phosphate, which is not readily soluble in water alone, but dissolves in solutions of several organic salts, and under some conditions, is available for the purposes of fertilization of plant crops. For some purposes, the addition of potassium salts to the fertilizer is necessary. These are usually added in the form of chloride or sulphate, which, under the name of **Stassfurt salts,** are largely imported for that purpose.

48. Preparation of Sample.—The sample should be well mixed, finely ground, and passed through a sieve having circular perforations 1 millimeter in diameter. The grinding and sifting should be performed as rapidly as possible, to avoid loss or gain of moisture during the operation.

DETERMINATION OF MOISTURE

49. As the percentage of moisture in a fertilizer may vary considerably under the conditions to which it is exposed, a determination of moisture is always necessary, in order that the results on other constituents, as determined by different analysts, as, for instance, those of the buyer and seller, may be fairly compared.

Some analysts invariably heat to a certain temperature (100° or 110°) until a constant weight is obtained; others heat for a certain time, 2, 3, or 5 hours, and call the loss *moisture*. The following plan, prescribed by the Association of Official Agricultural Chemists, is, however, probably most uniformly followed.

Potash salts, sodium nitrate, and ammonium sulphate are heated in quantities of 1 to 5 grams at about 130° until the

weight is constant, and the loss of weight is considered moisture. Of all other fertilizers, 2 grams, or should the sample be very coarse, 5 grams, are heated at 100° for 5 hours, and the loss considered moisture.

DETERMINATION OF PHOSPHORIC ACID

50. The phraseology regarding phosphoric acid in fertilizers is not always as exact as might be desirable. From what has been already stated, various forms of phosphoric acid are considered to exist, and, in fact, three forms are generally recognized in fertilizers, namely: (1) That readily soluble in water, consisting presumably of calcium superphosphate $CaH_4(PO_4)_2$. This is generally known as *soluble phosphoric acid*, or *water-soluble phosphoric acid.* (2) That not readily soluble in water, but soluble in certain organic solutions, presumably consisting of $CaH(PO_4)$, or acid ferric and aluminic phosphates. This form is usually called *reverted*, *inverted*, *reduced*, etc., *phosphoric acid;* or, because it is usually determined by washing it out with solution of ammonium citrate, it has been called *citrate soluble phosphoric acid.* (3) That insoluble both in water and in the solvents for (2), remaining presumably in the condition in which it originally existed in the phosphate rock, $Ca_3(PO_4)_2$. This form is either called *insoluble phosphoric acid* or *citrate insoluble phosphoric acid.*

The sum of (1) and (2) is usually termed *available phosphoric acid*, although English chemists apply the term "available" as a synonym for "water soluble," and, on the other hand, the term "soluble phosphoric acid" is sometimes used when the sum of (1) and (2) is meant.

Much of this confusion of terms has arisen from the diversity of opinion as to the utility of these different forms in which the phosphoric acid may be combined. The sum of (1), (2), and (3) is called *total phosphoric acid.*

51. Total Phosphoric Acid.—The phosphoric acid is usually separated as the molybdate compound, which is

dissolved in ammonia, and precipitated for weighing by magnesia mixture.

As the organic matter of the fertilizer would interfere with the complete separation of the phospho-molybdate, it must be destroyed (usually by the ignition with or without the addition of some nitrate). Hydrochloric acid is the best solvent for ignited phosphates, but the molybdate precipitation is best made in a nitric-acid solution, so that, although, after ignition, hydrochloric acid must be used to effect solution, nitric acid and nitrates should largely predominate when the molybdate separation is effected.

Weigh out 2 grams of the dried sample into a platinum dish and moisten these with 5 cubic centimeters of a magnesium-nitrate solution, made by dissolving 600 grams of magnesium nitrate in 1,000 cubic centimeters of water, and ignite. After cooling, add 5 to 10 cubic centimeters of hydrochloric acid and transfer the whole to a beaker; add 30 cubic centimeters of nitric acid, boil for a few moments, and filter.

When the fertilizers contain much iron and aluminum, more hydrochloric acid should be used. If made up with phosphatic slags, gelatinous silica will appear, which requires evaporation to dryness, and taking up with hydrochloric acid.

A method recommended for fertilizers containing very large quantities of organic matter, consists in boiling with 20 to 30 cubic centimeters of concentrate sulphuric acid in a Kjeldahl flask, adding 4 grams of sodium nitrate at the beginning of the digestion and a small quantity after the solution has become nearly colorless. After the solution is entirely without color, add 150 cubic centimeters of water, boil for a few minutes, and dilute. The presence of hydrochloric or sulphuric acid, however, retards the precipitation of the molybdate, and is best avoided, if possible. Hydrochloric acid can be removed by evaporating low with excess of nitric acid; sulphuric acid, however, cannot.

In any case, dilute the solution to 250 cubic centimeters, mix well, and remove, by means of a pipette, 50 cubic centimeters to a clean beaker for the analysis, this representing

.4 gram of the original sample. Add ammonia until it is just alkaline, then acidify by addition of 5 cubic centimeters of nitric acid; add 10 to 15 grams of crystallized ammonium nitrate, warm to about 85°, and add molybdate solution in the proportion of 50 cubic centimeters for every .01 gram of phosphoric acid assumed to be present. For ordinary fertilizers that contain less than 20 per cent. P_2O_5, 50 cubic centimeters will be quite sufficient. Digest for about an hour at 65° with frequent stirring, filter and wash with a cold dilute solution of ammonium nitrate, acidified with nitric acid. Test the filtrate for phosphoric acid by renewed digestion and addition of molybdate solution. Dissolve the precipitate on the filter with ammonia and hot water, and wash into a beaker to a bulk of not more than 100 cubic centimeters. Nearly neutralize this with hydrochloric acid, cool, and add magnesia mixture from a burette, slowly, about 1 drop per second, stirring vigorously. Let the whole stand for 15 minutes, and add 30 cubic centimeters of ammonia solution of .96 Sp. Gr. Let it stand for some time (2 hours is usually sufficient), and then filter and wash thoroughly with 2.5 per cent. NH_3, until practically free from chlorides. Burn the filter in a crucible, add the precipitate, ignite to whiteness, cool in a desiccator, and weigh as $Mg_2P_2O_7$.

52. Water-Soluble Phosphoric Acid.—Place 2 grams of the dry sample on a 9-centimeter filter, wash with successive small portions of water, allowing each portion to run through the filter before adding a new one, until the filtrate measures about 250 cubic centimeters. If the filtrate be turbid, add a little nitric acid. Make up to any convenient definite volume, mix well, remove 50 cubic centimeters and determine the phosphoric acid exactly as described in the preceding article.

53. Citrate-Insoluble Phosphoric Acid.—Heat 100 cubic centimeters of ammonium-citrate solution to exactly 65° in a flask placed in warm water, keeping the flask loosely stoppered. When this solution has reached 65°,

drop into it the filter containing the washed residue from the water-soluble determination, stopper tightly with a rubber stopper, and shake violently to reduce the paper to pulp. Return the flask to the warm water and maintain at exactly 65° for 30 minutes, shaking every 5 minutes. Filter, wash thoroughly with water at 65°. Return paper and contents to the flask, add 35 cubic centimeters of strong HNO_3 and 5 cubic centimeters of strong HCl, boil until all phosphate is dissolved. Dilute to 200 cubic centimeters, mix, filter through a dry paper, and determine the P_2O_5 in a definite volume of the filtrate. The sum of the water-soluble and citrate-insoluble subtracted from the total phosphoric acid, gives the citrate-soluble phosphoric acid.

54. Preparation of Ammonium-Citrate Solution. Ammonium-citrate solution is prepared by dissolving 370 grams of commercial citric acid in 1,500 cubic centimeters of water, nearly neutralizing this with commercial ammonia, and cooling. After cooling, more ammonia is added until the solution is exactly neutral, when the volume is made up to 2 liters. This solution should have a specific gravity of 1.09 at 20°.

DETERMINATION OF NITROGEN

55. Nitrogen is found in fertilizers both in the form of ammonia (potential and actual) and as nitrate. By potential ammonia is meant the nitrogen that, by the progress of decomposition of the organic matter of the fertilizer when in use, will develop ammonia. The nitrogen may be determined by one of the following methods:

56. Dumas's Method.—A definite amount of the sample is mixed with copper oxide in a combustion tube closed at one end, containing at the closed end a quantity of magnesium carbonate, which furnishes a supply of carbon dioxide with which to sweep out first the air and finally the products of the combustion from the tube. A roll of bright copper gauze is introduced near the open end to prevent the

escape of any nitrogen in the form of oxides of nitrogen. The tube is closed with a cork and delivery tube, and the nitrogen is collected in a measuring tube over caustic potash, whereby the carbon dioxide is removed.

A piece of combustion tube is drawn off and sealed at one end before the blowpipe. The tube should be about 76 centimeters long, or of such length that it can be heated to the extreme end when in the combustion furnace.

A quantity of magnesium carbonate (magnesite) is introduced, so that when the closed end is gently tapped on the bench, the salt shall occupy a space of about 20 centimeters. A layer of about 12 centimeters of pure, powdered copper oxide is introduced, the tube being conveniently supported by a clamp in a vertical position. About .5 gram of the fertilizer is carefully introduced into the tube, and, by means of a long, stout, clean wire, bent like a corkscrew at the end, is thoroughly stirred into the copper oxide below, to a distance of about one-half the depth of the copper oxide. A little more copper oxide (about $2\frac{1}{2}$ centimeters) is added, without withdrawing the wire, and the top layers of the lower stratum are mixed upwards into this. Once more a similar quantity of copper oxide is added, and the screw part of the wire thoroughly freed from any traces of the fertilizer by twisting up through this.

The tube is then filled to within 20 centimeters of the top with granular copper oxide, and a tolerably tight-fitting roll of bright copper gauze, 7 centimeters long, is introduced, then 7 centimeters granular copper oxide, and lastly a plug of asbestos. The tube is then removed from the clamp, and, while held in a horizontal position, it is gently tapped upon the bench. In this way the contents are made to settle down, so as to leave a narrow channel, or air space, all along the top. The tube is then placed into the combustion furnace.

A well-fitting cork with a bent delivery tube is inserted, and that middle portion of the tube containing the granular copper oxide is carefully heated to dull redness. As soon as the tube is visibly red hot, the most forward portions of the magnesium carbonate are heated so as to sweep out the air

from the tube by means of the CO_2 thus generated. Not more than about a little over one-third of the carbonate should be thus used at this stage.

As soon as the heating of the carbonate is commenced, the delivery tube is attached, by means of a rubber connection, to the lower branch tube of a Schiff's burette, as shown in Fig. 11. At the bottom of the burette, which is also known as an *azotometer*, there is previously introduced a small quantity of mercury, sufficient to reach about $\frac{1}{2}$ inch above the junction of the branch tube, and a strong solution of caustic potash (1 part of solid KOH in 2 parts of water) is poured into the movable reservoir *a*. The stop-cock *b* is then opened, and the burette filled with potash solution by raising the reservoir, after which the stop-cock is again closed, and the reservoir adjusted in about the position shown in the illustration. So long as air will still be expelled from the combustion tube, so long will gas collect in the burette; but, as it becomes swept out by the carbon dioxide, the ascending bubbles become smaller and smaller, until at last they are practically entirely absorbed by the potash solution. When this point is reached, the air that has collected is expelled by again cautiously raising the reservoir *a* and opening the stop-cock *b*, and the heating of the combustion tube extended first to the roll of copper gauze, and then gradually along the tube toward the mixture of copper oxide and the fertilizer.

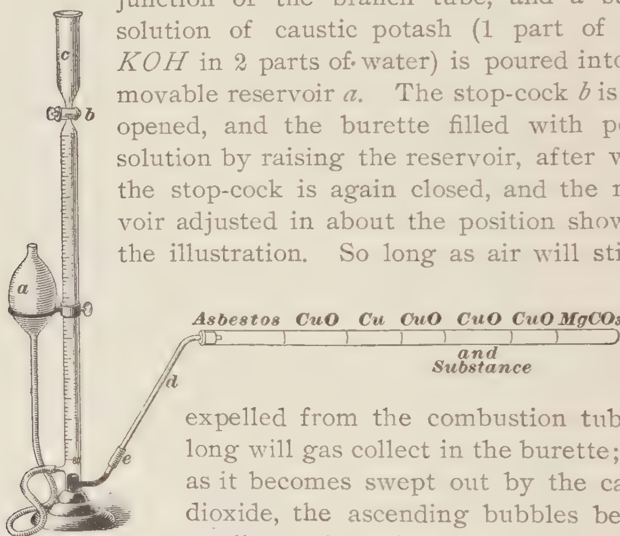


FIG. 11

The nitrogen that is evolved, together with the carbon dioxide now filling the air space of the tube, passes up into the burette, and the carbon dioxide being absorbed by the potash, the nitrogen alone collects. When the evolution

of nitrogen is completed, the remainder of the magnesium carbonate is heated, whereby a fresh supply of carbon dioxide is generated, which drives out the remainder of the nitrogen now filling the tubes. This is continued until the bubbles, which enter the burette through the mercury, are absorbed as before by the potash solution.

In order, however, to make quite sure that the carbon dioxide is completely removed, the cup *c* is filled with fresh potash solution, which is slowly admitted into the burette by cautiously opening the stop-cock. When the operation is completed, the delivery tube *d* is withdrawn from the rubber connector *e*, which is then closed with a pinch cock. The reservoir is raised until the surface of the liquid it contains is level with that in the burette, in which position the apparatus is left for about 15 minutes, to insure perfect absorption of any traces of carbon dioxide that may be present. The levels are then exactly adjusted, and the volume of the nitrogen read off upon the graduated tube.

The atmospheric temperature and pressure are noted, and the volume of gas reduced to normal temperature and pressure. As the tension of aqueous vapor exerted by such a strong solution of potash as is here used is considerably less than that of water alone, it is usual to give to p in the formula the value of half the tension of vapor of water, as given in the table.

Since 1 cubic centimeter of nitrogen, under normal conditions, weighs 1.254 milligrams, the weight in milligrams of nitrogen contained in that quantity of fertilizer employed for the analysis is obtained by multiplying the corrected volume, in cubic centimeters, by 1.254.

Thus, suppose the corrected volume of nitrogen = 50 cubic centimeters; then, the weight of nitrogen would be $50 \times 1.254 = 62.70$, from which the percentage may be readily obtained in the usual way.

57. Soda-Lime Process.—This method is based on the fact that many substances containing nitrogen, when strongly

heated with soda lime, give up their nitrogen in combination with hydrogen as ammonia. By estimating the ammonia so evolved, the weight of nitrogen can be determined.

The fertilizer is mixed with dry granulated soda lime in a combustion tube drawn to a point and closed at one end and containing a short layer of dry asbestos at its closed end. The drawn-out point should be long enough so that it may be easily broken at the end of the ignition. The evolved ammonia is absorbed in dilute acid contained in a Will and Varrentrap's bulb tube, which is attached to the combustion tube by means of a cork. The ammonia may be estimated either gravimetrically, by precipitation as ammonium platinum chloride, in which case the gas is absorbed in dilute hydrochloric acid (1 volume HCl to 4 volumes H_2O), and the estimation carried out as previously described, or it may be determined volumetrically by absorbing it in standard sulphuric acid, and titrating it with normal alkali as described under the heading Volumetric Determinations. The volumetric determination is the more rapid of the two, and hence mostly used.

Into the dry combustion tube, which should be from 40 to 45 centimeters long, is introduced a quantity of asbestos, previously rendered anhydrous by being heated to redness, sufficient to occupy about 5 centimeters. Upon this is added about the same quantity of dry, granular soda lime that has recently been moderately heated in a porcelain dish.

A quantity of soda lime, sufficient to occupy about 10 centimeters of the tube, is powdered in a dry porcelain mortar, and by means of a small spatula a weighed quantity of the fertilizer is thoroughly mixed with it. The mixture is then transferred to a sheet of clean paper and carefully poured into the tube. The mortar is then rinsed out with a little more powdered soda lime, which is also transferred to the tube. The tube will now be rather more than half full. Granular soda lime is added until it reaches to within about 5 centimeters of the mouth, and a plug of asbestos (previously heated to redness) is inserted to keep the materials in

position. The tube is then taped lengthwise on the table, in order to create a free air passage along the top of the materials, and is then laid in the furnace.

A measured volume of normal sulphuric acid, 15 to 25 cubic centimeters, depending on the capacity of the bulbs, is introduced into a Will and Varrentrap's bulb tube, shown in Fig. 12, which is then connected to the tube by a tight-fitting cork. The portion of the tube extending back from the asbestos plug, containing soda lime only, is first heated to a low redness, after which the heating is gradually extended along until the whole of the mixture of soda lime with the fertilizer has become heated. Regulate the heat so as to keep up a moderate and regular flow of gas through the bulbs.

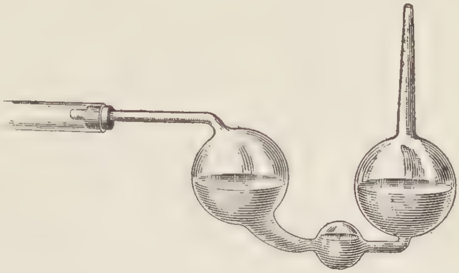


Fig. 12

Keep up the heat until gases have ceased bubbling through the acid in the bulbs, and the mixture of substance and soda lime has become white, or nearly so, which shows that the combustion is finished. The combustion should occupy about 45 minutes, but not more than an hour. Remove the heat, and when the tube has cooled below redness break off the closed tip and aspirate air slowly through the apparatus for 3 minutes.

In this way, the ammonia still filling the tube is driven out into the acid in the bulbs. The bulbs are then disconnected and the contents transferred to a beaker, the bulbs being thoroughly rinsed out with water. The excess of sulphuric acid present is titrated with normal sodium hydrate, according to the method previously described.

The attention of the student is called to the fact that the process should only be used for the determination of ammonia in the absence of nitrates.

58. Kjeldahl's Methods.—The most popular, and among the most accurate, methods for the determination of nitrogen are those originated by the Swedish chemist *Kjeldahl.* Two of his methods, as recommended by the Association of Official Agricultural Chemists, are here given; one is for the determination of nitrogen in the absence of nitrates, and the other for that in the presence of nitrates.

The apparatus needed for these determinations consists of the following: (1) Kjeldahl's digestion flasks. These are pear-shaped, round-bottom flasks, made of hard, moderately thick, well-annealed glass, having a total capacity of about 250 cubic centimeters. They are 22 centimeters long, and have a maximum diameter of 6 centimeters, tapering gradually to a long neck, which is 2 centimeters in diameter at the narrowest part, and flared a little at the edge. (2) Distillation flask and apparatus similar to that shown under Determination of Ammonium.

The reagents required are the following: (1) Standard sulphuric acid of known strength; half-normal acid is usually recommended. (2) Standard alkali solution, the strength of which should be relative to that of the sulphuric acid. (3) Ordinary sulphuric acid of Sp. Gr. 1.84; it must be chemically pure and especially free from nitrates and ammonium sulphate. (4) Metallic mercury or mercuric oxide. (5) Potassium permanganate which is used in a finely pulverized state. (6) Granulated zinc, pumice stone, or zinc dust; one of these reagents is added to the contents of the distillation flask, when found necessary, in order to prevent bumping. When zinc dust is used, .5 gram will usually be sufficient. (7) Potassium-sulphide solution, prepared by dissolving 40 grams of potassium sulphide in 1,000 cubic centimeters of water. (8) Sodium-hydrate solution; a saturated solution of chemically pure sodium hydrate. (9) Sodium thiosulphate. (10) Commercial salicylic acid. (11) A cochineal solution, prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cubic centimeters of strong alcohol and 200 cubic centimeters of distilled water for a day or two at ordinary

temperature, is used, after being filtered, as an indicator. This solution has a reddish or orange-yellow color, and turns violet-red on the addition of an alkali.

59. Determination in the Absence of Nitrates. From .7 to 3.5 grams of the substance to be analyzed, according to its proportion of nitrogen, are brought into a digestion flask with about .7 gram of mercuric oxide, or its equivalent in metallic mercury, and 20 cubic centimeters of sulphuric acid. The flask is placed in an inclined position and heated below the boiling point of the acid from 5 to 15 minutes, or until frothing has ceased. If the mixture froths badly, a small piece of paraffin may be added to prevent it. The heat is then raised until the acid boils vigorously. No further attention is required until the contents of the flask have become a clear liquid, which is colorless, or, at most, has a pale straw color. The flask is then removed from the flame, held upright, and, while still hot, potassium permanganate dropped in carefully and in small quantities at a time, until, after shaking, the liquid remains of a green or purple color.

After cooling, the contents of the flask are transferred to the distilling flask with about 200 cubic centimeters of water, a few pieces of pumice stone or granulated zinc, or .5 gram of zinc dust when found necessary to keep the contents of the flask from bumping, and 25 cubic centimeters of potassium-sulphide solution are added, with shaking. Next add 50 cubic centimeters of the soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the sides of the flask, so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 cubic centimeters will generally contain all the ammonia. This operation usually requires from 40 minutes to $1\frac{1}{2}$ hours. The distillate is then titrated with the standard alkali, using the cochineal solution as an indicator. Many prefer methyl orange to cochineal as indicator.

The use of mercuric oxide in this operation greatly

shortens the time necessary for digestion, which is rarely over $1\frac{1}{2}$ hours in case of substances most difficult to oxidize, and is usually less than 1 hour. In most instances, the use of potassium permanganate is unnecessary, but it is believed that in some cases it is required to complete oxidation, and, in view of this uncertainty, it is always used.

60. Kjeldahl's Method Modified to Include the Nitrogen of Nitrates.—Place from .7 to 3.5 grams of the fertilizer to be analyzed into a Kjeldahl digestion flask, add 30 cubic centimeters of sulphuric acid containing 1 gram of salicylic acid, and shake until thoroughly mixed, then add 5 grams of crystallized sodium thiosulphate, or add to the substance 30 cubic centimeters of sulphuric acid containing 2 grams of salicylic acid, then add 2 grams of zinc dust, shaking the contents of the flask at the same time. Finally, place the flask on the stand for holding the digestion flasks, where it is heated over a low flame until all danger from frothing has passed. The heat is then raised until the acid boils vigorously, and the boiling continued until white fumes no longer escape from the flask. This requires about 5 to 10 minutes. Add approximately .7 gram of mercuric oxide, or its equivalent in metallic mercury, and continue the boiling until the liquid in the flask is colorless, or nearly so. In case the contents of the flask are likely to become solid before this point is reached, add 10 cubic centimeters more of sulphuric acid. Complete the oxidation with a little potassium permanganate, as before, and proceed with the distillation and titration as described in the preceding article.

DETERMINATION OF POTASH

61. It is sometimes desirable to determine the potash in fertilizers, so the following method for different kinds of fertilizers is recommended by the Association of Official Agricultural Chemists:

62. Reagents Required in Potash Determination.
1. *Ammonium-chloride solution* is prepared by dissolving

100 grams of ammonium chloride in 500 cubic centimeters of water; to this, 5 to 10 grams of pulverized potassium platinic chloride are added, and the whole shaken at intervals for 6 or 8 hours. The mixture is allowed to settle overnight and filtered, and the residue is ready for the preparation of a fresh supply.

2. *Platinum Solution.*—The platinum solution used should contain 2.1 grams H_2PtCl_6 in every 10 cubic centimeters.

63. Methods of Dissolving the Fertilizer.—The following methods have to be employed according to the nature of the fertilizer under analysis:

(*a*) *With Potash Salts and Mixed Fertilizers.*—Boil 10 grams of the salt with 300 cubic centimeters of water 30 minutes. In the case of mixed fertilizers, add to the hot solution a slight excess of ammonia, and then sufficient powdered-ammonium oxalate to precipitate all the lime present. Cool, dilute to 500 cubic centimeters, mix and pass through a filter. In case of *muriate* and *sulphate of potash*, *sulphate of potash* and *magnesium*, and *kainite*, dissolve and dilute to 500 cubic centimeters without the addition of ammonia and ammonium oxalate.

(*b*) *With Organic Compounds.*—When it is desired to determine the total amount of potash in organic substances, such as cottonseed meal, tobacco stems, etc., saturate 10 grams with strong sulphuric acid, and ignite in a muffle at a low red heat, to destroy organic matter. Add a little strong hydrochloric acid, warm slightly, in order to loosen the mass from the dish, and proceed as directed in Art. **64** under (*a*).

64. Determination of Potash.—(*a*) *In mixed fertilizers*, evaporate 50 cubic centimeters of the solution, corresponding to 1 gram of the sample, nearly to dryness; add 1 cubic centimeter of dilute sulphuric acid (1 part H_2SO_4 and 1 part H_2O), evaporate to dryness, and ignite to whiteness. As all the potash is in the form of sulphate, no loss need be apprehended by volatilization of potash, and a full red heat must be maintained until the residue is perfectly white. Dissolve the residue in hot water, add a few drops of

hydrochloric acid and platinum solution in excess. Evaporate on the water bath to a thick paste, and treat the residue with 80-per-cent. alcohol, Sp. Gr. .8645. Wash the precipitate thoroughly with 80-per-cent. alcohol, both by decantation and on the filter, continuing the washing after the filtrate is colorless. Wash finally with 10 cubic centimeters of the ammonium-chloride solution mentioned in Art. **62,** 1, to remove impurities from the precipitate, and repeat this washing 5 or 6 times. Wash again thoroughly with 80-per-cent. alcohol, and dry the precipitate for 30 minutes at 100°.

(*b*) *Muriate of Potash.*—Dilute 25 cubic centimeters of the solution prepared according to the description under (*a*), Art. **63,** with 25 cubic centimeters of water, acidify with a few drops of hydrochloric acid, add 10 cubic centimeters of platinum solution, and evaporate to a thick paste. Treat the residue exactly as described under (*a*).

(*c*) *Sulphate of Potash, Sulphate of Potash and Magnesia, and Kainite.*—Dilute 25 cubic centimeters of the solution, prepared according to (*a*), Art. **63,** with 25 cubic centimeters of water, acidify with a few drops of hydrochloric acid, and add 15 cubic centimeters of platinum solution. Evaporate the mixture, and proceed as directed under (*a*), except that 25-cubic-centimeter portions of ammonium-chloride solution should be used for washing.

65. Factors.—For the conversion of potassium platinichloride to KCl, use the factor .3069; to K_2SO_4 .3587; and to K_2O .1939. It will be noticed that these factors differ slightly from those given in the table of factors. Those given here are the ones adopted by the Association of Official Agricultural Chemists.

66. Rapid Method of Determining Phosphoric Acid. The method of determining P_2O_5 by weighing as $Mg_2P_2O_7$ is recognized as the most accurate; but it must be carefully executed, and at best requires considerable time. On this account a volumetric method is very largely used. This method is much more rapid, and seems to be equally as

accurate. For total P_2O_5, treat 2 grams of fertilizer with 30 cubic centimeters of strong nitric acid and 5 cubic centimeters of strong hydrochloric acid. Boil until all organic matter is destroyed. Cool, dilute to 200 or 250 cubic centimeters, mix thoroughly, and filter through a dry paper. For samples containing below 5 per cent., take an amount of this filtrate corresponding to .4 gram of fertilizer; between 5 and 20 per cent., take an amount corresponding to .2 gram of fertilizer; and for over 20 per cent., take an amount corresponding to .1 gram of fertilizer. Transfer the measured portion to a 250-cubic-centimeter beaker. Add 7 cubic centimeters of nitric acid, make alkaline with ammonia, and then acid with nitric acid. Dilute to about 75 cubic centimeters, heat in a pan of water to from 60° to 65°, add 35 cubic centimeters of freshly filtered molybdate solution, stir well, and let stand at 60° to 65° for 15 minutes. Filter at once, wash, first by decantation, and then on the filter, until every trace of acid is removed. For this washing many chemists use a 3-per-cent. solution of potassium or ammonium nitrate; others, however, prefer cold distilled water. A paper may be used for filtering; but an asbestos filter as described under the determination of carbon in iron is more satisfactory. Transfer the filter with the yellow precipitate back to the beaker in which the precipitation was made, add about 30 cubic centimeters of water, then add from a burette an excess of standard sodium or potassium hydroxide, which must be free of carbonate; stir until the yellow precipitate is all dissolved, add .5 cubic centimeter of phenol-phthalein solution, and titrate the excess of alkali with standard nitric acid.

The same standard alkali and acid that were used in the determination of phosphorus in iron may be used here; but it is more convenient to have an alkali that is 32.38 per cent. normal, and an acid of either the same strength or exactly half this strength. One cubic centimeter of this alkali corresponds to .001 gram of P_2O_5. For water-soluble P_2O_5 and citrate-insoluble, dissolve as previously directed and take portions of the solutions corresponding to .2 or .4 gram, and proceed as in determining total P_2O_5.

PHOSPHATE ROCK

67. Phosphate rock, a valuable raw material for the manufacture of fertilizers, is found in various localities; especially valuable deposits are found in South Carolina, Florida, and Tennessee, where large quantities are mined not only for consumption at home, but also for export to Europe.

As the fertilizer manufacturer wishes to convert all of the calcium phosphate into the water-soluble acid phosphate, and as the oxides of iron and aluminum present "revert" part of the phosphoric acid, it is usually required of the phosphate miner that he guarantee that his product contains a certain minimum of calcium phosphate, or, as it is commonly called, bone phosphate of lime. This amount, of course, varies, but is seldom less than 50 per cent., and frequently higher than 80 per cent. A guarantee as to the maximum percentage of iron oxide and alumina is also generally demanded; this amount is often as low as 2.5 per cent. These figures are based on dry rock. The determinations usually necessary are moisture, which is necessary in order to make the other calculations on a "dry basis," P_2O_5 from which the bone phosphate of lime is calculated, Fe_2O_3 and Al_2O_3.

68. Determination of Moisture.—Weigh 3 grams of finely powdered sample into a weighed porcelain crucible, heat in an air bath at 110° for 2 hours, cool, weigh, and calculate the moisture from the loss of weight.

69. Determination of Phosphoric Anhydride. Treat 1 gram of powdered sample in a flask with 30 cubic centimeters of strong nitric acid and 7 cubic centimeters of strong hydrochloric acid. Heat until brown fumes cease to come off, add 25 cubic centimeters of water, cool, dilute to a definite volume, mix, filter through a dry paper, and take a measured quantity of the liquid, corresponding to 1 gram if the volumetric method is to be used, or .2 to .5 gram if

the gravimetric method is to be used. Determine the P_2O_5, as directed under Fertilizers. The percentage of P_2O_5 multiplied by 2.1831 gives the percentage of bone phosphate of lime.

70. Determination of Iron Oxide and Alumina. Take 10 grams of the sample, transfer to a flask, add 50 cubic centimeters of strong hydrochloric acid, heat on the water bath for 30 minutes, cool, dilute to 500 cubic centimeters, mix, without filtering, take 25 cubic centimeters (corresponding to .5 gram of the sample), add 2 drops of methyl-orange solution, and then ammonia drop by drop until a faint precipitate appears; but the solution remains acid, as shown by the methyl orange. Now add 15 cubic centimeters of a 33-per-cent. solution of sodium acetate, which has been made faintly acid with acetic acid. Place the beaker containing the solution in a pan of water that is kept at exactly 72° for 5 minutes, filter, wash twice with water, at 70°, which contains a little ammonium acetate. Dissolve the precipitate in hydrochloric acid, and wash the paper free of iron. To this hydrochloric-acid solution add 4 cubic centimeters of a 5-per-cent. solution of ammonium phosphate. Repeat the precipitation with sodium acetate exactly as before, filter, wash, and dissolve as before. Precipitate a third time, proceeding as before, but using ammonium acetate instead of sodium acetate. Filter, wash six times with dilute ammonium acetate. Ignite in a porcelain crucible and weigh. This precipitate consists of $AlPO_4$ and $FePO_4$. It may be dissolved in hydrochloric acid and the iron determined volumetrically. Then from the amount of iron found the amount of $FePO_4$ is calculated; this deducted from the weight of the precipitate gives the weight of $AlPO_4$, which, multiplied by .41851, gives the weight of Al_2O_3. The amount of iron found multiplied by 1.42859 gives the amount of Fe_2O_3. From these figures calculate the percentages. It is generally easier instead of dissolving the precipitate of $AlPO_4$ and $FePO_4$ to determine the iron in a measured quantity of the original solution.

71. Some phosphate rock contains considerable pyrite FeS_2. Part of this may be dissolved by digesting with strong hydrochloric acid and thus be calculated as Fe_2O_3. It is to the interest of the phosphate miner to show as small an amount of Fe_2O_3 as possible, and the chemist is sometimes asked to determine pyrite as well as iron oxide. To make a really accurate determination of the iron existing in these two forms would involve a complete analysis of the rock, a procedure out of the question in commercial work. The following method, however, generally gives results sufficiently accurate:

Use measured quantities of the solution made up for the determination of phosphoric acid for the determination of Al_2O_3 and Fe_2O_3, using the methods already described, but remembering that the nitric acid must be removed before determining the iron volumetrically. In this way the Al_2O_3 is determined, and the total Fe_2O_3, that is the Fe_2O_3 existing as such in the rock, and that which could be formed from the pyrite present. Now to determine the actual Fe_2O_3, take 2 grams of the sample in a flask, add 75 cubic centimeters of water and 25 cubic centimeters of strong hydrochloric acid. Heat rapidly to boiling, cool by placing the flask in cold water. Dilute to 200 cubic centimeters, mix, filter through a dry paper, and determine the iron volumetrically in an aliquot part of the filtrate. The dilute acid used here should not attack the pyrite, and the iron got is that existing as oxide. From the iron found here calculate the percentage of Fe_2O_3, and report as actual Fe_2O_3. From the total Fe_2O_3 subtract the actual Fe_2O_3; multiply the remainder by 1.5, which gives the FeS_2.

72. Determination of Sulphur in Pyrite and Pyrite Cinder.—The sample should be in an impalpable powder, which is best got by grinding in an agate mortar. Weigh 1 gram of this powder into a small flask, which then has a small funnel placed in its neck. Add 15 cubic centimeters of strong nitric acid, 5 cubic centimeters of strong hydrochloric acid, and .5 cubic centimeter of pure bromine. Let stand cold for 15 minutes, then heat on a water bath for

2 hours. Then add 25 cubic centimeters of strong hydrochloric acid, and continue heating on the water bath until all is dissolved except a small amount of silica, which should be white. Cool, dilute slightly, filter, and wash the solution from the paper, using as little water as possible. To the clear filtrate add ammonia until it is nearly neutral, boil, and add ammonia in slight but distinct excess. To the boiling alkaline solution, which will contain a precipitate of $Fe(OH)_3$, add slowly, at the rate of 2 drops a second, 20 cubic centimeters of a hot 10-per-cent. solution of barium chloride. Continue boiling 2 minutes after all the barium chloride is added. Then add slowly a slight excess of hydrochloric acid, and boil 1 minute after all the $Fe(OH)_3$ is dissolved. Let stand for 2 hours, filter, wash, ignite in a platinum crucible, cool, add 3 drops of H_2SO_4, ignite again, cool, weigh, and calculate the percentage of sulphur from the weight of the $BaSO_4$.

ANALYSIS OF SOAP

PRELIMINARY REMARKS

73. Soaps are mainly alkali salts of fatty acids; in fact, sodium and potassium salts. Soda soaps are hard and come into the market under the name of *compact*, *cut*, or *filled* soaps. Potash soaps are soft, and are known as *soft soaps*. Lately, however, hard potash soaps have appeared. For analytical purposes, soap may be classified as follows: *Toilet soaps*, the best grades of which are free from impurities and free alkali. *Laundry soaps*, containing generally an excess of alkalies, in the form of either sodium silicate, sodium carbonate, or free alkali, and resin. *Commercial soaps*, the great variety of soaps used in the arts and industries; this class may be subdivided into (*a*) *soft soaps*, in which potash is the base, and (*b*) *hydrated soaps*, in which soda represents the base, being formed by caustic soda and palmnut oil or cocoanut oil. *Medicated soaps*, containing medicinal agents, such as carbolic acid, sulphur, tar, etc.

74. The complete analysis of a soap frequently presents considerable difficulty, since many adulterants may be used in the cheaper grades and many substances not adulterants, the use of which is permitted as colorants and perfume. It has been stated that besides the alkali and fatty acids and water requisite for the formation of a soap, the following substances have been found in the different varieties, namely, ocher, ultramarine, sodium aluminate, borax, resin, vermilion, arsenite of copper, alcohol, sugar, vaseline, camphor, gelatine, petroleum, naphthalene, carbolic acid, tar, glycerine, bran, starch, etc.

75. Sampling of Soap.—In analyzing soaps, care must be taken to obtain a fairly representative sample. In the case of hard soap, this is best effected by cutting a transverse slice from the middle of the bar or cake. A cylinder withdrawn from a cake by means of a cork borer or cheese sampler, also affords a fairly good sample. In many cases, it is preferable to reduce the soap to thin slices or shavings, which should be thoroughly mixed and preserved in a well-stoppered bottle.

DETERMINATION OF WATER

76. The determination of the proportion of water in soap is important, and requires considerable care to insure accurate results. If the soap is solid, a fairly representative sample should be reduced to fine shavings or scraping with a knife. A known weight is then exposed for some time to a temperature of 40° to 50°, the heat being gradually raised to 100°, and continued at that temperature as long as loss in weight is observed. The soap should not be allowed to melt.

A more rapid method that is also applicable in cases of soft soap, consists in placing from 5 to 10 grams of the sample, finely divided in the case of hard soap, into a large porcelain crucible, set in a sand bath that is heated by a small Bunsen flame. The soap is continually stirred with a glass rod (weighed with the crucible) having a roughed and jagged

end, a peculiarity that greatly facilitates the stirring and breaking up of the lumps of soap formed toward the end of the operation. The operation is usually complete in 20 to 30 minutes, and is known to be at an end when a piece of plate glass placed over the crucible (the flames being removed) is no longer bedewed with moisture. Care is required, however, to prevent burning of the soap, but the odor thus developed is so characteristic that the manipulation is easily controlled.

The proportion of water in soap varies greatly; in so-called dry soaps, it rarely exceeds 16 to 20 per cent., while in inferior soaps, made from cocoanut oil, it sometimes reaches 70 to 80 per cent.

DETERMINATION OF UNSAPONIFIED MATTER

77. For the determination of unsaponified matter, the soap that has been dried by one of the processes described in the preceding article is extracted in an extraction apparatus, similar to that described in the analysis of milk with petroleum ether, which, for that purpose, should boil below 80°, and leave no residue on evaporation. After the extraction is complete, the petroleum ether is distilled off, the residue dried at 100°, and weighed.

In a boiled, well-made soap, there should be no unsaponified matter, unless the same has been added subsequently. In addition to unsaponified fats, foreign matters are sometimes found in the petroleum-ether extract, such as soft paraffin (so-called mineral soap stock), waxes, phenol, etc.

DETERMINATION OF TOTAL ALKALI AND FATTY ACIDS

78. The portion of the soap not volatile at 100° and insoluble in petroleum ether, really constitutes the *soap proper*, and is dissolved in hot water preparatory to determining the total alkali and fatty acids therein.

In analyzing soap of known origin and general composition, it is often unnecessary to go through the previous operations

of drying and exhausting with petroleum ether. In such cases, it is evidently preferable to weigh out 10 grams of the original soap and at once treat it with hot water.

A pure soap dissolves completely in hot water, and no ordinary product should leave more than a slight residue. If the soap under examination is so-called "scouring soap," the insoluble residue will be found to contain quantities of fine sand. The residue, if appreciable, should be washed by decantation, and eventually brought upon a filter with hot water, dried at 100°, and weighed, after which, if deemed desirable, it can be subjected to further examination.

79. To the aqueous solution is added an excess of half-normal sulphuric acid, setting free the fatty acids that rise to the surface. The beaker in which the precipitation was effected is next cooled by placing it in ice water, thus solidifying the fatty acids. When the fatty acids have solidified, it is best to decant the liquid, remelt with hot water 2 or 3 times to remove any enclosed mineral acid, cool again, filter, and wash with cold water until the washings are no longer acid, as shown by litmus.

The filtrate from the insoluble fatty acids contains the total alkali now present as sulphate, the excess of sulphuric acid and any glycerol, which may have been present in the soap if saponification has been effected in the cold. The acid liquid may further contain a small quantity of soluble fatty acids. It is first titrated with half-normal potassium hydrate, using methyl orange as an indicator. From the original amount of half-normal sulphuric acid added, and from the number of cubic centimeters of half-normal potassium hydrate required to neutralize the excess of the same, the total alkali of the sample is calculated and reported as Na_2O.

After the liquid has been rendered neutral to methyl orange (which indicates the mineral acid), phenol-phthalein solution is added and more potassium hydrate is run in. The number of cubic centimeters of potassium hydrate required

for neutralizing the phenol-phthalein solution corresponds to the quantity of soluble fatty acids present, thus:

$$C_7H_{15}CO_2H + KOH = C_7H_{15}CO_2K + H_2O$$

and this is calculated to caprylic anhydride $\begin{matrix} C_7H_{15}CO \\ C_7H_{15}CO \end{matrix}{>}O$, in the absence of more definite knowledge as to their nature. The calculation is made by simple proportion, thus:

molecular weight of $C_7H_{15}CO_2H$: molecular weight of

$$\begin{matrix} C_7H_{15}CO \\ C_7H_{15}CO \end{matrix}{>}O = \text{weight of } C_7H_{15}CO_2H : x$$

In soaps containing silicates of the alkalies (a not unusual constituent), the gelatinous silicic acid that separates on the addition of sulphuric acid remains with the fatty acids on filtration. To separate the fatty acids from this, as well as other impurities, it is advisable to proceed as follows:

The funnel containing the filter, with the fatty acids, is placed in a small beaker and heated in an air bath. As the filter dries, the fatty acids pass through it and collect in the beaker below, while all impurities, silicic acid, talc, etc., remain on the filter. Of course, it is necessary to wash the filter, which remains saturated with the fatty acids, with hot alcohol or petroleum ether. The alcohol or petroleum ether is distilled off and the residue treated in the same way as described above.

DETERMINATION OF FREE ALKALI

80. For the determination of **free alkali**, a separate portion of the sample is weighed out, and extracted in an extraction apparatus with neutral alcohol. The caustic alkali is determined in the alcoholic solution by titrating with half-normal hydrochloric acid, using phenol-phthalein as an indicator. If, however, soap contains unsaponified fat, as is quite frequently the case when the soap is made by the so-called *cold process*, this method cannot be used, since in alcoholic solution, unsaponified fat would be readily saponified by the free caustic alkali present. In such a case, the soap must be dried first in an atmosphere free from carbon

dioxide at 100°, the unsaponified matter extracted with petroleum ether, and finally the soap dissolved in alcohol and the free alkali determined in the alcoholic solution, as before. The sodium carbonate, sodium silicate, borax, and everything insoluble in alcohol, remains behind in the extraction tube, and may be tried at 100°, and weighed. If considerable, it may be further treated as follows:

The residue is exhausted with boiling water, and the solution is then titrated with half-normal hydrochloric acid, using methyl orange as an indicator. The amount of acid required corresponds to carbonate, silicate, and borate, which are reported together.

DETERMINATION OF RESIN

81. Resin is a very common constituent of soaps, the resinates of the alkalies having a similar action to soaps, and the cheapness of the material naturally suggesting a partial substitution of it for the natural fats and oils. As a qualitative test for resin, Gottlieb's method is usually employed.

82. Gottlieb's Qualitative Test for Resin.—A small quantity of the soap under examination is dissolved in water and heated to boiling. A strong solution of magnesium sulphate is added until the fatty acids are completely precipitated. The magnesium resinates remain in solution. After boiling 2 or 3 minutes, the solution is filtered and the hot filtrate acidified with dilute sulphuric acid. In the presence of resin, the liquid becomes turbid, due to the separated resin acids. The boiling should be continued for ½ hour, to make sure that the turbidity is due to resin acids and not to volatile fatty acids.

83. Hübl's Method of Quantitative Determination of Resin.—From ½ to 1 gram of the solid mixture of fatty and resin acids, obtained as previously described, is heated in a closed flask on the water bath with 20 cubic centimeters of alcohol to complete solution. The acids are neutralized with alkali, using phenol-phthalein as an indicator.

The alcoholic-soap solution is then poured into a beaker, the flask rinsed with water, the solution diluted to about 200 cubic centimeters, and silver nitrate added to complete precipitation. The precipitate, consisting of the silver salts of resin and fatty acids, must be protected from sunlight. It is filtered off, washed thoroughly with water, dried at 100°, and extracted in an extraction apparatus with ether. The silver resinates dissolve in the ether, while the silver salts of the fatty acids remain undissolved. The ethereal solution of the resin acids should have a yellow or light-brownish color. It is filtered, if necessary, and the filtrate shaken with hydrochloric acid in a separatory funnel. The resulting ethereal solution of resin acids is filtered from the silver chloride, washed with water, and the filter and separator rinsed with ether, the ether distilled off, and the residue dried at 100°, and weighed.

As the resin is weighed in the hydrated form, its weight must be multiplied by the factor .9732 to obtain the weight of the anhydride.

84. In most analyses of soap, the following determinations are made: Water, alkali combined as soap (as Na_2O), alkali free (as sodium hydrate), sodium carbonate, and total fatty acids as anhydrides. The composition of an ordinary yellow laundry soap is given below:

Water	19.26
Alkali combined as soap Na_2O	8.57
Alkali free as $NaOH$	0.20
Alkali as Na_2CO_3	0.20
Fatty anhydrides	52.32
Resin	19.45
Total	100.00

DETERMINATION OF SUGAR

PRELIMINARY REMARKS

85. The different varieties of sugar, their constitution, properties, etc., are treated under the heading Carbohydrates in *Organic Chemistry*, and, in order to get a better understanding of what will be said in this Section, the student is advised to study, in conjunction with these methods of analysis, the articles coming under that heading.

The investigation of sugar and saccharine products, such as beets, the juice, molasses, etc., extends as a rule to the estimation of cane sugar, invert sugar, water, alkalinity, and ash.

DETERMINATION OF CANE SUGAR

86. Cane sugar may be determined from the specific gravity or by polarization.

87. Specific Gravity.—It is evident that an accurate estimation of sugar in solution, by means of the specific gravity of the solution, can only be executed if no other dissolved substances are present. Should other substances be in solution, they affect the specific gravity in different ways. In such solutions, only an apparent value expressed in per cent. of sugar can be obtained.

The determination of specific gravity is conducted either with one of the usual forms of applicable apparatus, such as pycnometer, hydrostatic balance, densimeter, in which case the percentage of sugar corresponding to the specific gravity must be referred to in a corresponding table, or by means of an areometer specially constructed for the purpose, the saccharimeter of *Brix* or *Balling*. The object of the Balling or Brix instrument is to give in direct percentages the solid

matter in solution. It is evident that for this purpose the instrument must be graduated for a particular kind of material, since 10 per cent. of sugar in solution might have a different specific gravity from a similar quantity of another body. Instruments of this kind, graduated for pure sugar, are found very useful in technical sugar analysis. To attain greater accuracy and avoid an instrument with too long a stem, the Brix hydrometer is made in sets. A convenient arrangement is to have a set of three, graduated as follows: one from 0° to 30°, one from 25° to 50°, and one from 45° to 85°. When the percentage of solid matter dissolved is over 70, the readings of the scale are not very reliable. These instruments, similar to the Baumé hydrometer, are graduated at a fixed temperature, usually 17.5°; special tables, showing the corrections to be applied to the scale reading when made at any other temperature, are usually supplied with the instruments. A certain amount for every degree of temperature and every 5 per cent. of solids has to be subtracted or added, according as the temperature is below or above 17.5°.

88. Optical Properties of Natural Sugars.—As has been already stated in the Sections on *Physics* and *Organic Chemistry*, the solutions of all natural sugars have the property of deflecting the plane of polarized light, and the degree of deflection corresponds to the quantity of sugar in the solution. By measuring the amplitude of the rotation produced, the percentage of sugar in the solution can be determined. In order to secure accuracy in the determination, it is necessary that only one kind of sugar be present, or, if more than one, that the quantities of all but one be determined by other means, and the disturbances produced thereby in the total rotation be properly arranged. As a matter of fact, the process in practice is applied chiefly to cane and milk sugars, both of which occur in nature in an approximately pure state.

The instruments used for measuring the degree of deflection produced in a plane of polarized light is called a *polariscope*, *polarimeter*, or *saccharimeter*. For a theoretical

discussion of the principles of polarization, and the application of these principles in the construction of saccharimeters, the student is referred to Sections on *Physics*, and to standard works on optics and the construction of optical instruments. For the needs of the student, a description of the instruments most commonly used and the method of using them will be sufficient.

89. The Saccharimeter.—A **saccharimeter,** or **polariscope,** for the solutions of sugar, consists essentially of a prism for polarizing the light, called, as has been previously mentioned, a **nicol,** a tube of definite length for holding the sugar solution, a second nicol made movable on its axis for adjustment to the degree of rotation, and a graduated arc for measuring it. Instead of having the second nicol movable, many instruments have an adjusting wedge of quartz of opposite polarizing power to the sugar, by means of which the displacement produced on the polarized plane is corrected. A graduated scale and vernier serve to measure the movement of the wedges and give in certain conditions the desired reading of the percentage of the sugar present. Among the large number of instruments that have been constructed for analytical purposes, only three are generally used in this country, and these will be described here.

The simplest form of a polarizing instrument consists of two nicol prisms, one of which, namely, the analyzer, is capable of rotation about its long axis. The prolongation of this axis is continuous with that of the other prism, i. e., the polarizer. The two prisms are sufficiently removed from each other to allow the interposition of the polarizing body, in a tube of definite length, the polarizing power of which is to be ascertained.

For purpose of description, three kinds of saccharimeter may be mentioned:

1. Instruments in which the deviation of the plane of polarization is measured by rotating the analyzer about its axis.

Instruments of this type conform to the simple type just mentioned and illustrated in *Physics ;* they are under most

conditions the best as well as the cheapest. The *Laurent*, *Wilt*, *Landolt-Lippich*, etc. belong to this class.

2. Instruments in which nicols are stationary, and the direction of the plane of polarized light collected by the interposition of a wedge of a solid polarizing body.

To instruments of this type belong those of *Soleil*, *Duboscq*, *Scheibler*, and the compensating apparatus of *Schmidt and Haensch*.

3. Apparatus in which the analyzer is set in a constant angle with the polarizer, and the compensation secured by varying the length or concentration of the interposed polarizing light.

The apparatus of *Trannin* belongs to this class.

90. Appearance of Field of Vision.—Saccharimeters are also classified in respect to the appearance of the field of vision as follows:

1. Tint instruments, the field of vision of which in every position of the nicols, except that on which the plane of vibration of the polarized light is coincident with the three principal sections, is composed of two semidisks of different color.

2. Shadow instrument, where the field of vision in all, except neutral positions, is composed of two semidisks, one dark and one yellow. As the neutral position is approximated, the two disks gradually assume a light yellow color, and when neutrality is reached, they appear to be equally colored.

The *Laurent*, *Schmidt and Haensch shadow*, and *Landolt-Lippich* instruments belong to this class.

3. Striated instruments, where the field of vision is striated. The lines may be tinted as in the *Wild polaristrobometer*, or black, as in the *Duboscq* and *Trannin* instruments. The neutral position is indicated, either by the disappearance of the striæ (Wild's), or by the phenomenon of their becoming continuous (Duboscq's and Trannin's).

91. Light Employed in the Use of Polariscopes. Polariscopes may further be distinguished as those that are

used with white light (oil lamp, etc.), and those that are used with monochromatic light (sodium flame, etc.). The Scheibler and the Schmidt and Haensch apparatus belong to the first class, while the Laurent and Landolt-Lippich apparatus belong to the second class.

Some of the instruments in common use are arranged to be used with ordinary lamps or gas light, and also with a monochromatic flame. Laurent's polarimeter is one of this kind.

92. Rotation Instrument.—This instrument has already been described as one in which the extent of deviation in the plane of polarization, caused by the intervention of an optically active substance, is measured by rotating one of the nicols about its axis, and measuring the degree of this rotation by a vernier on a graduated arc.

93. Laurent Polariscope.—A polariscope adapted by Laurent to the use of monochromatic yellow light is largely used in this country. It has the second nicol, called the *analyzer*, movable, and the degree of rotation produced is read in angular terms directly from a divided circle. The scale is graduated both in angular measurements and in per cent. of sugar for a definite degree of concentration of the solution and a definite length of the observation tube. The normal solution for this instrument contains 16.9 grams of pure sugar in 100 centimeters, and the length of the observation tube is exactly 200 millimeters. Both the angular rotation and the direct percentage of sugar can be read at the same time. The light is rendered yellow by bringing into the flames of a double Bunsen burner spoons made of platinum wire, which carry small pieces of fused sodium chloride.

94. Construction of Laurent's Polariscope.—The shadow polariscope invented by Laurent is constructed as follows: The polarizer is a special nicol that is not fixed in its position, but is so arranged that it turns about its own axis. By this device, the quantity of light passing through it can be regulated and the apparatus is thus useful with

colored solutions that are not easily cleared by any of the common bleaching agents. The greater the quantity of light admitted, however, the less delicate the reading of the shadow produced. The plane of polarized light emergent from this prism falls on a disk of glass half covered with a thin lamina of quartz that thus divides the field of vision into halves. It is this semidisk of quartz that is the distinguishing feature of the apparatus. The polarized light thus passes without hindrance the half field of vision that is covered by the glass only, but cannot pass the quartz plate unless its axis is set in a certain way. The field of vision may be thus half dark, or both halves may be equally illuminated or equally dark, according to the position of the nicol analyzer, which is freely movable about its axis and carries a vernier and reading glass over a graduated circle. The field of vision in the Laurent apparatus may have the following forms. Let the polarizer be first so adjusted that the plane of polarization of the transmitted pencil of light is parallel to the axis of the plate lying in the direction $A\ B$, Fig. 13. The two halves of the field of vision will then

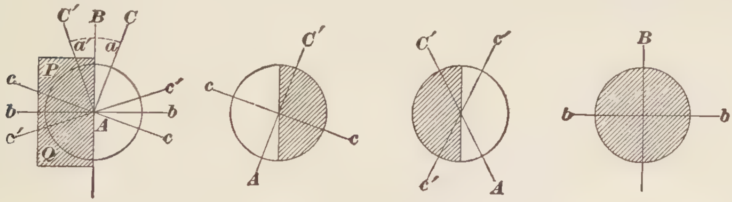


FIG. 13

appear equally illuminated in every position of the analyzer. But, if the polarizing nicol is inclined to $A\ B$ at an angle a, the plane of polarization of the rays passing through the quartz plate will undergo deviation, through an angle in the opposite direction.

It happens from this, that when in the uncovered half of the field, the plane of polarization has the direction $A\ C$, in the other half it will have $A\ C'$. When the analyzer is rotated, if its plane of polarization lie in the direction $c\,c$, the rays polarized parallel to $A\ C$ will be completely extin-

guished and the corresponding half of the field will be dark. The opposite happens when the plane of polarization lies in the direction of $c' c'$. When one half of the field is thus obscured, the other half suffers only a partial diminution of the intensity of its illumination. When the middle position $b\,b$ is reached in the rotation of the analyzer, the illumination of the two halves is uniform, and this is the point at which the zero of the scal is reached. The slightest rotation of the analyzer to the right or left of this neutral point will cause a shadow to appear on one of the halves of the field, which, by an oscillatory movement of the analyzer, seems to leap from side to side. The smaller the angle a or $B\,A\,C$, the more delicate will be the shading and the more accurate the observation.

The various pieces composing the polariscope are arranged

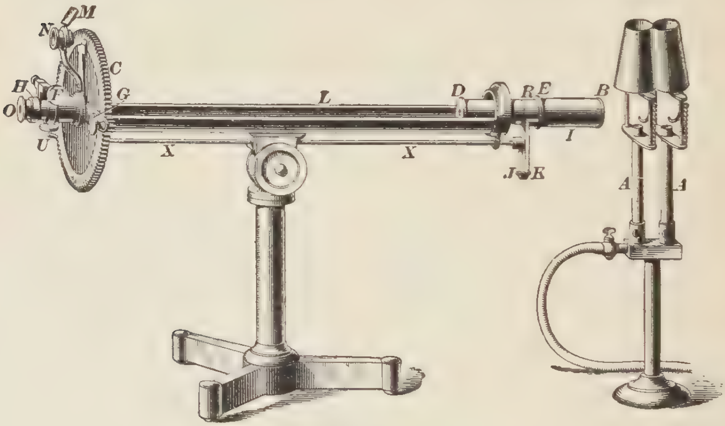


FIG. 14

in the following positions, beginning on the right of Fig. 14, and passing to the left, where the observer is seated:

1. The lamp $A\,A$.

2. The lens B for condensing the rays and rendering them parallel.

3. The tube I, blackened inside to carry the lens.

4. A thin lamina E, cut from a crystal of potassium bichromate, serving to render the sodium light more mono-

chromatic. When the saccharine liquid under examination is colored, this crystal is removed before observation is made.

5. The polarizer *R*, which is rotatable through a small angle by the lever *K*.

6. The lever *J K*, for rotating the tube containing the polarizer. This is operated by the rod *X* extending to the left.

7. Diaphragm *D*, half covered with a lamina of quartz.

8. Trough *L* for holding the observation tube.

9. Disk *C*, carrying divided circle and sugar scale.

10. Mirror *M*, to throw the light of the lamp on the vernier of the scale.

11. Reading glass *N*, carried on the same radius as the mirror, and used to magnify and read the scale.

12. Device *F*, to regulate the zero of the instrument.

13. Tube *H*, carrying a nicol analyzer and ocular *O* for defining the field of vision. This tube is rotated by the radial arm *G*, carrying the mirror and reading glass.

95. Manipulation.—The lamp having been adjusted, the instrument, in a dark room, is so directed that the most luminous spot of the flame is in the line of vision. An observation tube filled with distilled water is placed in the trough and the zero of the vernier is placed accurately on the zero of the scale. The even tint of the field of vision is then secured by adjusting the apparatus by the device mentioned in No. 12, Art. **94.**

96. Soleil-Ventzke Polariscope.—A form of polariscope giving a colored field of vision has been constructed, that of Soleil-Ventzke being most exclusively used in this country. This instrument is very accurate and capable of rendering very good service, especially in the hands of those that have a delicate perception of color.

The general arrangement of a tint instrument, as modified by Scheibler, is shown in Fig. 15. Beginning to the right of the figure, its optical parts are as follows: *A* is a nicol, which, with the quartz plate *B*, forms the apparatus for

producing the light-rose neutral tint. The proper degree of rotation of these two parts is secured by means of the button *L* attached to the rod carrying the ratchet wheel as shown. The polarizing nicol at *C* and *D* is a quartz disk, one-half of which is right-handed, and the other left-handed. At *G*

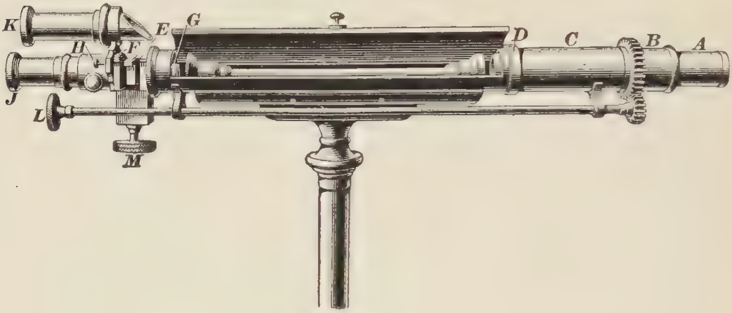


FIG. 15

is another quartz plate belonging to the analyzing part of the apparatus. This, together with the fixed quartz wedge *F* and the movable quartz wedge *E*, constitute the compensating apparatus of the instrument whereby the deviation produced in the plane of polarized light by the solution in the tube is restored.

Next to the compensation apparatus is the analyzing nicol, which, in this instrument, is fixed in a certain place, viz., the zero of the scale. The analyzer and the telescope for observing the field of vision are carried in the tube *HJ*. The movable quartz wedge has a scale that is read with a telescope *K*, provided with a mirror inclined at an angle of 45°, just over the scale, and serving to illuminate it. The quartz wedges are also provided with a movement by which the zero point of the scale can be adjusted. A kerosene lamp with two flat wicks is the best source of illumination, and the instrument should be used in a dark room and the light of the lamp, save that which passes through the instrument, be suppressed by a shade. The sensitive or transion tint is produced by that position of the regulating apparatus that gives a field of view of such nature that a given small

movement of the quartz compensation wedge gives the greatest contrast in color between the halves of the field of vision. For most eyes, a faint rose-purple tint, as nearly colorless as possible, possesses this quality. A slight movement of the quartz wedge by means of the screw head *M* will, with this tint, produce on one side a faint green and on the other side a pink color, which are in strong contrast. The neutral point is reached by so adjusting the quartz wedge as to give both halves of the field the same faint rose-purple tint.

97. Shadow Polariscope for Lamp Light.—Shadow polariscopes have recently come into use for saccharimetric work. They possess on the one hand, the advantages of those instruments using monochromatic light, and on the other, the ease of manipulation possessed by the tint instruments. A shadow polariscope differs from the tint instrument in dispensing with the nicol and quartz plate used to regulate the sensitive tint, and in having its polarizing nicol

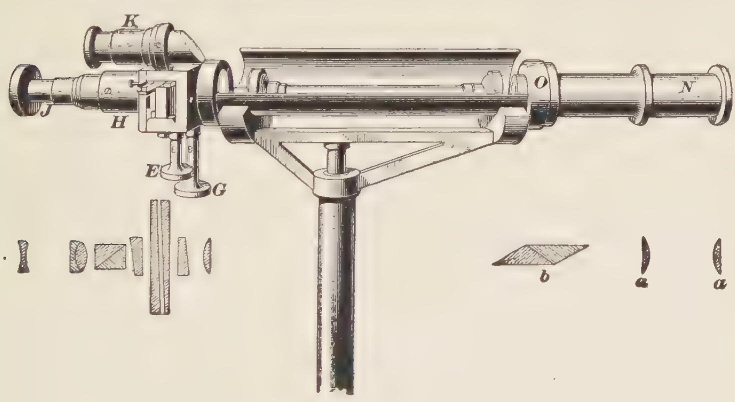


FIG. 16

peculiarly constructed. The more improved forms of the apparatus have a double quartz-wedge compensation. The two wedges are of opposite optical properties, and serve to make the observation more accurate by mutual correction. The optical arrangement of the different parts of such an apparatus is shown in Fig. 16.

The lenses *a*, *a* for concentrating the rays of light and rendering them parallel are contained in the tube *N*. At *O* is placed the modified polarizing nicol *b*. The two compensating quartz wedges are moved by the milled screw heads *E*, *G*. The rest of the optical apparatus is arranged as described under the tint polariscope in Art. **96.**

98. When properly made, all the instruments that have been mentioned are capable of giving accurate results, if used according to the minute directions supplied with each instrument. In the use of polariscopes having colored fields of vision, a delicate sense of distinguishing between related tints is necessary to do good work; color-blind persons obviously cannot use this kind of apparatus successfully; in the shadow instruments, it is only necessary to distinguish between the halves of a field of vision unequally illuminated, and reduce this inequality to zero. A neutral field is thus secured of one intensity of illumination, and of only one color, usually yellow. Such a field of vision permits of the easy discrimination between the intensity of the coloration of its two halves, and is consequently not trying to the eye of the observer, and allows great accuracy of discrimination.

The manipulation of the polariscope can only be properly learned by using it, and the student, if he follows the direction accompanying each apparatus, with a little practice will soon be able to use it efficiently.

The normal weight for most apparatus equals 26.048 grams; that is, a solution of 26.048 grams of pure cane sugar in 100 cubic centimeters in a tube 200 millimeters in length causes a rotation of 100°, or 1° corresponds with .26048 gram of sugar in 100 cubic centimeters. With the use of this normal weight and a normal tube (200 millimeters) the percentage of sugar can consequently be read off directly. When a 100-millimeter or a 400-millimeter tube is used, the degrees are to be doubled or halved.

99. Preparing Sugar Solution for Polarization. Polarization is always preceded by clarification and decolori-

zation, as a perfectly limpid liquid is of great importance to secure accurate observations. For this purpose, a solution of basic lead acetate is usually employed. This solution acts as a clarifying agent by throwing out of solution certain organic compounds and, by uniting with the organic acids in solution, forms an additional quantity of precipitate, and these precipitates act also mechanically in removing suspended matter from solution. The action of this reagent is therefore very effective for clarification purposes.

The reagent most frequently employed is of the following strength: $1\frac{1}{2}$ liters of water, 464 grams of lead acetate, and 264 grams of litharge are boiled for half an hour, with frequent stirring. The solution is then allowed to cool, diluted to 2 liters, allowed to settle, and the clear solution, after being decanted, is ready for use. The specific gravity of this solution is approximately 1.267.

To 100 cubic centimeters of the sugar solution, 10 cubic centimeters of this solution are added, the precipitate is allowed to settle, and then filtered off, and the thus clarified solution is ready for polarization.

100. Errors Due to Use of Lead-Acetate Solution. In the use of lead solutions, there is some danger of errors intruding into the results of the work. These errors are due to various sources. Lead subacetate solution, when used with low-grade products, or sugar juices, or syrups from beets and canes, precipitates albuminous matter and also the organic acids present. The bulk occupied by these combined precipitates is often of considerable magnitude, so that on completing the volume in the flask, the actual sugar solution present is less than indicated. The resulting condensation tends to give too high results. With purer samples, this error is of no consequence, but especially with low-grade syrups and molasses it is a disturbing factor that must be considered.

One of the best methods of correcting it has been proposed by Scheibler, and is as follows:

To 100 cubic centimeters of a solution of a sample, 10 cubic centimeters of the lead subacetate solution are added, and

after shaking and filtering, the polarimetric reading is taken; another quantity of 100 cubic centimeters of the solution with 10 cubic centimeters of the lead solution is diluted to 220 cubic centimeters, shaken, filtered, and polarized. Double the second reading, subtract it from the first, multiply the difference by 2.2, and deduct the product from the first reading. The remainder is the correct polarization. Attention is here called to the fact that cane sugar is dextrorotary (+), while invert sugar is levorotary (–).

EXAMPLE.—The first polarization of a sugar solution is 30.0, the second, 14.9. What is the true percentage of sugar in the solution?

SOLUTION.—

$$30 - (2 \times 14.9 = 29.8) = .2$$
$$.2 \times 2.2 = .44$$
$$\text{and } 30 - .44 = 29.56. \quad \text{Ans.}$$

INVERT SUGAR

101. Invert Sugar.—Invert sugar possesses the property of reducing Fehling's solution with separation of cuprous oxide Cu_2O. On the basis of this precipitated cuprous oxide, which is reduced to metallic copper, the amount is determined by a method that will be described later. The results obtained by polarization are influenced by the levorotary power of invert sugar. Therefore, in the presence of the latter, a different procedure, that of Clerget, is followed in the estimation of cane sugar. The description of this is given further on.

WATER

102. Water.—The use of small, flat-bottomed porcelain or enameled sheet-iron dishes is recommended for fluid or semifluid products. Drying is done on a water bath or in an air bath at 80° to 90°, and the temperature gradually raised to 105° until constant weight is obtained.

Some chemists prefer to mix the substance (4 to 5 grams molasses, 8 to 10 grams syrup and dense juices) with 20 grams ignited quartz sand, free from dust, in a small porcelain dish. This is weighed, including a small glass stirring rod, and placed in an air bath at 100° for 15 minutes.

It is then removed from the air bath, stirred with the rod until a homogeneous mass is obtained, and again placed in the air bath and dried to constant weight.

ALKALINITY

103. Alkalinity.—This is influenced by the presence of free alkali, lime, and free ammonia in the saccharine substance. It is estimated by titration with normal, or one-tenth normal, acid, and is usually calculated into per cent. of lime. Neutral, bluish-violet litmus tincture, which is added to the liquid, is used as indicator, but in the analysis of dark-colored substances, such as molasses, the indicator is not added, but instead, after each addition of acid, the liquid is tested with a strip of bluish-violet litmus paper. Phenol-phthalein may be used instead of litmus.

ASH

104. Ash.—The residue left on ignition of a sugar, including the mechanically admixed impurities in the same, is called the **ash.** The residue of sugar free or freed from these impurities is called the **salts.** The latter consists mainly of alkali sulphates or chlorides and carbonates arising from salts of organic acids. Potassium predominates in these alkalies, but calcium carbonate, arising from soluble organic calcium salts, is also frequently found. These salts form a serious obstacle to the complete crystallization of the sugar, and hence cause a loss in the yield.

The complete ignition of sugar is not readily accomplished, since easily fusible alkali salts withhold small particles of carbon from combustion, and too strong a heat might cause the volatilization of alkali chlorides. The incineration is, therefore, conducted as follows: The weighed sugar is charred in a spacious platinum dish until gas is no longer evolved. The coke is then moistened with water and crushed to a paste with a pestle. After the addition of a little hot water, and heating, the mixture is filtered and the residue thoroughly washed on the filter with hot water, and

the filter and residue, after being dried, incinerated in the platinum dish. The filtrate added to this is evaporated to dryness on a water bath, moistened with ammonium carbonate, dried at 100°, and moderately ignited. The clean white residue is weighed.

In this way the *ash*, or, as it is sometimes called, the *carbonate ash*, is ascertained. If the estimation of *salts* is needed, a weighed quantity of sugar is dissolved in water, usually 25 grams of sugar in 250 cubic centimeters of water. The turbid solution is filtered, and a definite quantity of the filtrate is evaporated in a platinum dish, charred, and heated, as before.

105. Scheibler's Method for Determining Ash. A simpler and quicker method for the determination of ash has been recommended by Scheibler, as is seen by the following: For this purpose, from 3 to 5 grams of sugar are moistened with sulphuric acid in a platinum dish. After a few minutes, the sugar blackens and is decomposed. It is then heated over a very large flame, whereby thorough charring takes place with much swelling, hissing, and gas evolution. To completely burn off the remaining coke, the dish is placed in a muffle.

The action of sulphuric acid converts the salts into sulphates, the weight of which is naturally higher than that of the salts originally present. The increase of weight equals almost exactly 10 per cent., by which the weight found must be decreased. The remainder is reported as carbonate ash.

ANALYSIS OF SUGAR BEETS

EXTRACTION OF SUGAR

106. Scheibler Extraction Method.—A fine paste is prepared by rasping a cross-section of the beet sample, by hand or machine. Of this paste, 35 to 40 grams are weighed out as quickly as possible on a weighed pan and placed in the

cylinder *a* of a Soxhlet extractor, shown in Fig. 17. In the wide-mouthed 100-cubic-centimeter flask *b*, with which the apparatus is provided, 75 cubic centimeters of absolute alcohol are placed. The residue on the pan is rinsed into the cylinder with absolute alcohol, and then sufficient of the latter is added to fill the cylinder almost to the top of its siphon *c*. The flask *b* is attached to the apparatus, and heated until extraction is completed. This takes, as a rule, 3 to 4 hours, in which time, the alcohol will be siphoned 80 to 90 times. The water bath, on which the bottle *b* has been resting, is withdrawn, the flask is allowed to cool, and a sufficient quantity of lead acetate, 5 to 10 cubic centimeters, is added. It is then diluted to the mark, well mixed by shaking, and polarized in a 200-millimeter tube.

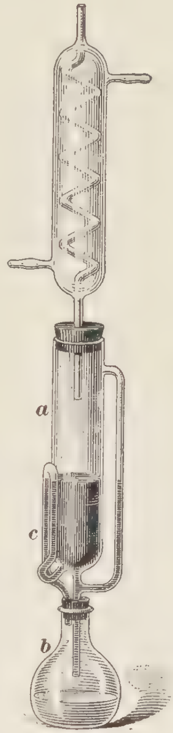


FIG. 17

The rotation observed, multiplied by .26048, gives the amount of sugar contained in the weighed paste, from which the percentage is readily obtained. If 26.048 grams of beets are used, then direct percentages of sugar are obtained.

107. Digestion Method of Rapp and Degner. — Like Scheibler's method, this one depends on an alcohol extraction, the difference being that 52.096 grams, double the normal weight that is used, are directly placed in a graduated flask of exactly 200 cubic centimeters capacity. The flask is marked down low and is provided with a widened neck, into which a condenser, about 50 centimeters in length and 10 millimeters in diameter, can be ground or securely fastened with a tight-fitting cork. Charging is done with a glass rod, and the particles adhering to this, to the pan, and to the neck of the pan, are washed in with a wash bottle containing 90 to 92 per cent. alcohol. The flask is filled to four-fifths its capacity with the same

strength alcohol. After adjusting the condenser, the flask is placed in an inclined position on a water bath already heated to boiling, and the contents of the former are kept in ebullition for 15 to 20 minutes. The sugar is thereby completely dissolved in the liquid. The flask is removed, the condenser washed with alcohol, and filled about 1 cubic centimeter above the mark, without cooling. By successive immersions into the hot water bath, to a point where ebullition begins, a thorough mixture is obtained. It is thereupon allowed to cool in the air for $\frac{1}{2}$ to $\frac{3}{4}$ hour, and is finally brought to the temperature of the room by immersing in water. To the liquid, which has sunk down below the mark, 10 to 15 drops of lead acetate are added. It is then diluted to the mark with alcohol, well mixed by shaking, filtered, and polarized. The readings made with the use of a 200-millimeter tube yield direct percentages. In order to compensate, however, for the extracted pulp left in the flask, the result obtained is multiplied by .994. The true percentage is thus obtained.

108. Pellet's Method of Cold Diffusion.—The impalpable pulp of the beet having been obtained by rasping a cross-section of a beet, the contents of sugar therein is determined as follows:

A normal or double-normal quantity, i. e., 26.048 grams or 52.096 grams, of the pulp is quickly weighed, in a sugar dish shown at (*a*), Fig. 18, and washed into a sugar flask (*b*), Fig. 18, which should be graduated, as shown in the illustration, to allow for the volume of the fiber, or marc, of the beet. Since the beet pulp contains, on an average, 4 per cent. marc, the volume which is

(*a*) (*b*)

FIG. 18

occupied thereby is assumed to be a little more than 1 cubic centimeter. Since it is advisable to have as large a volume as convenient, Pellet recommends to wash the pulp into a flask graduated at 201.35 cubic centimeters. If a 200-cubic-centimeter flask is used, the weight of the pulp should be 25.87 grams instead of 26.048 grams. After the pulp is washed into the flask, about 6 cubic centimeters of lead acetate, having a specific gravity of 30° Baumé, are added together with a little ether, to remove the foam. The flask is now gently shaken and water added to the mark, and the contents thoroughly shaken up. If the pulp has been rasped or grated finely enough, the filtration and polarization may follow immediately. The filter into which the contents of the flask are poured should be large enough to hold the whole quantity at once. If 26.048 grams have been taken, the volume diluted to 201.35 cubic centimeters, and the liquid polarized in a 200-millimeter tube, the percentage of sugar can be read off directly.

It is not necessary to heat the solution in order to insure complete diffusion, but the temperature at which the operation is conducted should be the ordinary one of the laboratory. In case the pulp is not as fine as it should be, the flask should be allowed to stand for half an hour after filling, before filtration. An insufficient amount of lead acetate may permit some rotary bodies other than sugar to pass into solution, and care should be taken always to have the proper quantity of the clarifying material added.

109. Analysis of Beet Juice.—The beet under examination is grated on an ordinary grater and about a pint of the pulp placed in the cylinder of the press shown in Fig. 19. Pressure is applied, and the thus extracted juice flows into a beaker under the spout. The juice is then poured into a tall cylindrical glass, its temperature noted, and the density observed by means of a Brix hydrometer. Of this juice, 100 cubic centimeters are then transferred by means of a pipette to a sugar flask having two graduations, one at 100 cubic centimeters and one at 110 cubic

centimeters. It is filled to the latter mark with lead acetate, and thoroughly shaken up. Clarification and decolorization are effected after a few minutes. It is then filtered and polarized in a 200-millimeter tube. The angle read off is increased by one-tenth, because of the dilution with lead acetate, and this is then multiplied by .26048. The volume percentage—the grams of sugar in 100 cubic centimeters—is thus obtained. Should the percentage by weight be desired, it is only necessary to divide the first result by the specific gravity observed by means of the hydrometer.

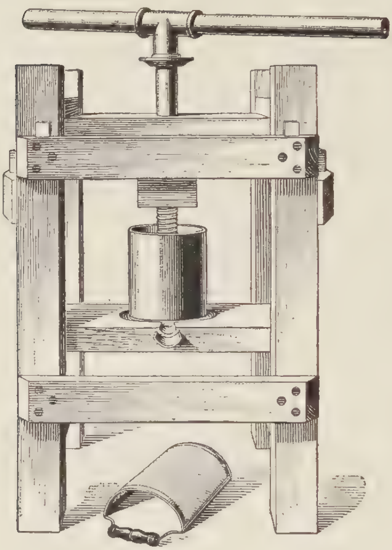


FIG. 19

The following determinations are usually reported:

1. *Per Cent. of Total Solids in the Juice.*—This is obtained by means of the hydrometer.

2. *The Percentage of Sugar in the Juice.*—This is determined by means of the polariscope, as has been described.

3. *The Percentage of Sugar in the Beet.*—The percentage of sugar in the beet is obtained by multiplying the percentage of sugar in the juice by $\frac{95}{100}$.

4. *Percentage of Purity of a Juice.*—This term is often called the *coefficient of purity* or the *quotient of purity*. It expresses the ratio between the per cent. of total solids in the juice and the per cent. of sugar in that same juice. That is, in any particular juice, the purity expresses what proportion of the total solids is sugar. It is obtained by dividing the per cent. of sugar in the juice by the per cent. of total solids, and multiplying by 100.

The term purity is not an indication of the quality of a

juice, but the quality of the total solids in the juice; that is, it tells how many parts are sugar in every 100 parts of solids.

Below is the average of 496 samples analyzed by the writer in one season:

Per cent. solids in juice	18.30
Per cent. sugar in juice	15.29
Per cent. sugar in beet	14.53
Per cent. purity	83.60

RAW SUGAR, FILLING MATERIAL, GREEN SYRUP, AND MOLASSES

110. Analysis.—In the preceding articles, directions have been given for the estimation of sugar (sucrose or saccharose) by its optical properties. It has been assumed so far, that no other disturbing bodies have been present, save those that could be removed by means of clarifying agents. The case differs, however, when two or more sugars are present, each of which has a specific relation to polarized light. In such cases, some method must be used for the optical determination of sucrose that is independent of the influence of the other polarizing bodies, or else recourse must be had to other methods of analysis. The conversion of the sucrose present into invert sugar by the action of an acid or a ferment, affords an opportunity for the estimation of sucrose in mixed sugars, by purely optical methods. This process rests upon the principle that by the action of a dilute acid for a short time, or of a ferment for a long time, the cane sugar is completely changed, while other sugar present is not sensibly affected. Neither of these assumptions is rigidly correct, but each is practically applicable (see *Organic Chemistry*).

The cane sugar by this process of hydrolysis is converted into an equal mixture of glucose and fructose, as is seen from the following equation:

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underbrace{\underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}}_{\text{inverted sugar}}$$

The former, at room temperature, has the higher specific rotating power, and the deflection of the plane of polarization in a solution of inverted sugar is therefore to the left. The levorotary power of invert sugar varies with the temperature, and this arises from the optical properties of the levulose or fructose. The influence of temperature on the rotating power of other sugars is not imperceptible in all cases, but in practice is negligible.

Since the rotating power of levulose diminishes as the temperature rises, an accurate thermometric observation must accompany each polarimetric reading.

111. Qualitative Test for Invert Sugar.—Before estimating quantitatively, cane sugar in syrups, molasses, raw sugar, etc., a qualitative test for invert sugar has to be made, as the way of procedure, for the reasons given above, differs according to the presence or absence of invert sugar.

To test, qualitatively, for invert sugar, 20 grams of the substance under examination are dissolved in water, clarified by means of lead acetate, and the volume brought up to 100 cubic centimeters; 50 cubic centimeters of the clarified and filtered solution are mixed with an equal volume of Fehling's solution, placed on a piece of wire gauze on a tripod, heated to boiling, and kept boiling for 2 minutes. The formation of cuprous oxide signifies the presence of invert sugar, and the estimation of the cane sugar has to be made according to Art. **113,** while in the absence of cuprous oxide and consequently that of invert sugar, the cane-sugar determination is made according to Art. **112.**

112. Estimation of Cane Sugar in the Absence of Invert Sugar.—The normal weight, i. e., 26.048 grams, of the substance under examination, is dissolved in a flask graduated at 100 cubic centimeters, 2 to 3 cubic centimeters

of lead acetate, and 1 to 2 cubic centimeters of alum solution are added, and the volume increased to 100 cubic centimeters. The contents of the flask are thoroughly shaken, and then filtered. The filtrate is poured into a 200-millimeter tube and polarized, when the direct percentage of cane sugar can be read off.

Alumina in the form of a thin hydrate paste is frequently substituted for lead acetate, when pure sugars are used. The action of the alumina paste or cream is wholly mechanical, and, therefore, leaves the sugars in solution unchanged, carrying out only suspended matter. It is prepared by dissolving commercial aluminum chloride in 100 volumes of water and precipitating with ammonia to alkaline reaction. The precipitated aluminum hydrate is allowed to settle, the supernatant liquid is drawn off, and the precipitate washed by decantation until alkaline reaction ceases. The hydrate is suspended in pure water in proportions to produce a creamy liquid. The cream thus prepared is shaken just before using, and from 1 to 5 cubic centimeters of it, according to the degree of turbidity of the saccharine solution, are added before the volume in the flask is completed to the mark. After filling the flask to the mark, the ball of the thumb is placed over the mouth of the bottle, and the contents well shaken and allowed to stand for a few moments before filtering.

When lead acetate is used as clarifying agent it is advisable to neutralize the alkaline reaction and destroy the slight turbidity still remaining, by introducing a glass rod moistened with concentrate acetic acid.

113. Estimation of Cane Sugar in the Presence of Invert Sugar.—This process of estimation of cane sugar in the presence of invert sugar is based on the observations of Clerget and published in 1846 in the proceedings of the Society of Encouragement for National Industry.

He points out first the observations of Mitcherlich regarding the influence of temperature on the rotary power of invert sugar, and calls attention to the detailed experiments he has

made that resulted in the determination of the laws of the variation. From these studies, he was able to construct a table of correction, applicable in the analysis of all saccharine substances in which the cane sugar is polarized before and after inversion. The basis of the law rests on the observation that a solution of pure sugar, polarizing 100° on the sugar scale before inversion, will polarize 44° * to the left after inversion at a temperature of 0°. The quantity of sugar operated on by Clerget amounted to 16.471 grams in 100 cubic centimeters of liquid. On the polariscope employed by him, this quantity of sugar in 100 cubic centimeters gave a reading of 100° to the right on the sugar scale when contained in a tube 200 millimeters long. This process has been modified in many ways since; the modified detailed process, which the writer has found to give accurate result, is carried out as follows:

Half the normal quantity, i. e., 13.024 grams, of the substance under examination is dissolved with 75 cubic centimeters of water in a flask graduated at 100 cubic centimeters; 5 cubic centimeters of hydrochloric acid, Sp. Gr. 1.188, are added and the solution diluted to the mark. The mouth of the flask is then closed with the thumb and its contents shaken to mix it thoroughly. A thermometer is placed in the flask, which is set in a water bath in such a way that the water comes above the level of the liquid in the neck of the flask. The water is heated in such a manner as to bring the temperature of the contents of the flask, as determined by the thermometer, exactly to 68°, and at such a rate as to require 15 minutes to reach this result. At the end of 15 minutes, the temperature having reached 68°, the flask is removed and immediately placed in another water bath at the temperature of the room, to which temperature the contents of the flask is cooled as rapidly as possible. It is then poured into a 100-millimeter polarization tube by means of a tubulure in its center, which serves not only the purpose of filling the tube, but also to carry the thermometer afterwards, by means of which the temperature of observation

* Later investigations give 42.66° instead of 44°.

can be taken. The polarization is then observed. The result is doubled if a 200-millimeter tube is taken. After the sugar has been inverted, the liquid shows a strong levorotary power ($-I°$).

In addition to this determination, polarization as described in Art. **112** is carried out with a separate sample in the usual manner ($+P°$).

114. Calculation of the Results.—If S equals the sum of the angle of polarization before and after inversion (omitting the negative sign of the invert sugar), that is, $P° + I°$, and $t°$ equals the temperature of observation in centigrade degrees, then the cane sugar R can be calculated from the formula

$$R = \frac{100\,S}{142.66 - \frac{1}{2}\,t°} \qquad (2)$$

This formula is based on the fact that pure cane sugar, which, as has been already stated, rotates 100° before inversion, shows after inversion a rotation of $42.66 - \frac{t°}{2}$. Therefore, the decrease of rotation of pure sugar is $142.66 - \frac{t°}{2}$.

EXAMPLE.—Let the polarization before inversion be $+95°$, after inversion $-26°$, and the temperature 20°.

SOLUTION.—Using formula **2** and substituting the known values, we obtain:

$$R = \frac{100 \times (95 + 26)}{142.66 - 10},$$

or $$R = \frac{12,100}{132.66} = 91.21 \text{ per cent. of cane sugar.} \quad \text{Ans.}$$

115. Estimation of Invert Sugar.—When the presence of invert sugar has been established by means of the qualitative test given in Art. **111**, before determining its quantity finally, an approximate quantitative test has to be made. This is done by dissolving 10 grams of the substance in water, clarifying it with an appropriate amount of lead acetate, filtering and diluting the mixture to 100 cubic centimeters. Each cubic centimeter of this solution contains

.1 gram of the original substance, and 10, 8, 6, 4, and 2 cubic centimeters of it are placed in separate test tubes, 5 cubic centimeters of Fehling's solution are added to each, and the contents are then boiled. Notice is taken of the tube whose contents are nearly decolorized. Should this be the case, for instance, with the one containing 10 cubic centimeters, there is less than 1.5 per cent. of invert sugar present, and the final determination is conducted according to the method of Herzfeld (see Art. **116**). In the other case, the method of Meissl and Hiller is employed (see Art. **118**). For the latter method, the number of cubic centimeters in that test tube which is nearly decolorized gives simultaneously the number of grams that, dissolved in 50 cubic centimeters, are used in the final determination.

Every cubic centimeter of sugar solution (10 grams in 100 cubic centimeters) corresponds to .1 gram of substance. But in the method of Meissl and Hiller, 10 times the amount of Fehling's solution (50 cubic centimeters) is used; hence, 10 times the quantity of sugar is also taken, and, consequently, every cubic centimeter of solution in the preliminary test represents 1 gram of substance in the latter determination.

Should the test, therefore, show that decolorization took place with 8 cubic centimeters, but that with 6 cubic centimeters a blue tint remained, then 6 grams dissolved in 50 cubic centimeters of water are used.

116. Herzfeld's Method of Estimating Invert Sugar.—A solution, clarified with lead acetate containing the normal weight (26.048 grams) of the substance in 100 cubic centimeters, is used. This is precipitated with sodium carbonate when any great excess of lead acetate has been used. In case precipitation with sodium carbonate is not necessary, 38.4 cubic centimeters of filtered solution, diluted to 50 cubic centimeters, which would correspond to 10 grams of the substance, are used. When, however, precipitation with sodium carbonate is necessary, 46.07 cubic centimeters

of solution, diluted to 60 cubic centimeters with concentrate sodium-carbonate solution, are withdrawn and filtered; 50 cubic centimeters of the filtrate are then employed, and these also correspond to 10 grams of the substance under examination.

These 50 cubic centimeters are placed in an Erlemeyer flask or a dish, together with 50 cubic centimeters of Fehling's solution, and heated with a large burner to boiling. That moment is accepted as the beginning of ebullition when bubbles arise from the sides as well as from the bottom of the containing vessel. The flame of the burner is then somewhat reduced and the boiling continued for exactly 2 minutes. After the expiration of 2 minutes, the vessel is removed from the flame, 100 cubic centimeters of cold water (previously boiled) are added and the contents are rapidly filtered, with the aid of a filter pump, on a weighed asbestos filter, shown in Fig. 20. The precipitate is rapidly washed, first by decantation and then on the filter, using altogether about 300 to 400 cubic centimeters of hot water; this is followed by a washing with about 20 cubic centimeters of alcohol, finally by one with ether, and then the tube is dried in an air bath at 120° to 130°.

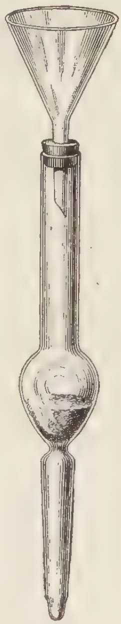


FIG. 20

The portion of the tube containing the cuprous oxide on the filter is next heated to a low, red heat to oxidize and destroy all organic matter, and is then reduced to metallic copper by heating slowly in a current of hydrogen. Reduction requires only moderate heat and is complete in a few minutes. It is allowed to cool in hydrogen, and the water collected in the neck is allowed to evaporate. It is then placed in a desiccator and weighed after 15 minutes. The invert sugar is gotten from the amount of reduced copper by means of Table III.

TABLE III

TABLES OF HERZFELD

Copper. Milligrams	Invert Sugar. Per Cent.	Copper. Milligrams	Invert Sugar. Per Cent.	Copper. Milligrams	Invert Sugar. Per Cent.	Copper. Milligrams	Invert Sugar. Per Cent.
50	.05	120	.40	190	.79	260	1.19
55	.07	125	.43	195	.82	265	1.21
60	.09	130	.45	200	.85	270	1.24
65	.11	135	.48	205	.88	275	1.27
70	.14	140	.51	210	.90	280	1.30
75	.16	145	.53	215	.93	285	1.33
80	.19	150	.56	220	.96	290	1.36
85	.21	155	.59	225	.99	295	1.38
90	.24	160	.62	230	1.02	300	1.41
95	.27	165	.65	235	1.05	305	1.44
100	.30	170	.68	240	1.07	310	1.47
105	.32	175	.71	245	1.10	315	1.50
110	.35	180	.74	250	1.13		
115	.38	185	.76	255	1.16		

117. The following details are yet to be considered: The asbestos must be proof against acids and alkalies, and should be previously ignited. It is then suspended in water, poured on the glass wool in the tube, and pressed with a glass rod having a flattened end, so that a thin but perfectly solid layer that filters without the use of the pump is formed. It is then washed with alcohol, dried, and weighed. During filtration, a short, thick funnel is loosely placed on the tube, but, while washing, the latter is replaced by a funnel attached tightly to the tube by means of a rubber stopper, as is shown in Fig. 20. The liquid in the tube should not be allowed to run off entirely while washing. The hydrogen used in reducing must be free from arsenic. The tube is attached to the drying bottle by a glass and rubber tube in a tight-

fitting rubber stopper, and is inclined upwards, as shown in Fig. 21. Instead of using glass wool to rest the asbestos on

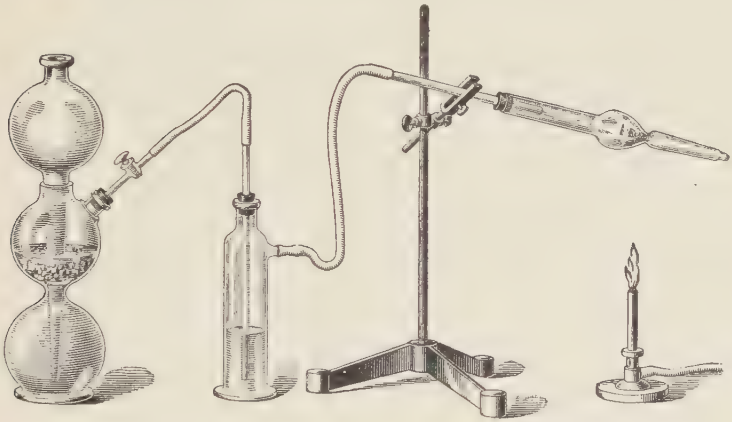


FIG. 21

in the filter tube, a perforated platinum disk is very convenient.

Instead of asbestos filter, filter paper washed with hydrofluoric acid may be used. In this case, likewise, 300 to 400 cubic centimeters of hot water are used in washing. It is then incinerated, placed in a Rose crucible, covered with the perforated lid, and reduced in hydrogen.

118. Meissl and Hiller's Method for Estimating Invert Sugar.—This method is generally used when the amount of invert sugar exceeds 1.5 per cent. The necessary quantity of substance for analysis is determined from the above mentioned experiments (see Art. **115**). In order to obtain this dissolved in 50 cubic centimeters, double the quantity is weighed out, brought into solution, and the volume made up to 100 cubic centimeters. It is clarified, filtered, and 50 cubic centimeters of the filtrate are used. With this quantity, the estimation of invert sugar is conducted in the same way as in the Herzfeld method.

TABLE IV

MEISSL AND HILLER'S FACTORS FOR THE DETERMINATION OF MORE THAN 1.5 PER CENT. OF INVERT SUGAR

Ratio of Cane Sugar to Invert Sugar $= R:I$	$I =$ 200 milligrams	$I =$ 175 milligrams	$I =$ 150 milligrams	$I =$ 125 milligrams	$I =$ 100 milligrams	$I =$ 75 milligrams	$I =$ 50 milligrams
0:100	56.4	55.4	54.5	53.8	53.2	53.0	53.0
10:90	56.3	55.3	54.4	53.8	53.2	52.9	52.9
20:80	56.2	55.2	54.3	53.7	53.2	52.7	52.7
30:70	56.1	55.1	54.2	53.7	53.2	52.6	52.6
40:60	55.9	55.0	54.1	53.6	53.1	52.5	52.4
50:50	55.7	54.9	54.0	53.5	53.1	52.3	52.2
60:40	55.6	54.7	53.8	53.2	52.8	52.1	51.9
70:30	55.5	54.5	53.5	52.9	52.5	51.9	51.6
80:20	55.4	54.3	53.3	52.7	52.2	51.7	51.3
90:10	54.6	53.6	53.1	52.6	52.1	51.6	51.2
91:9	54.1	53.6	52.6	52.1	51.6	51.2	50.7
92:8	53.6	53.1	52.1	51.6	51.2	50.7	50.3
93:7	53.6	53.1	52.1	51.2	50.7	50.3	49.8
94:6	53.1	52.6	51.6	50.7	50.3	49.8	48.9
95:5	52.6	52.1	51.2	50.3	49.4	48.9	48.5
96:4	52.1	51.2	50.7	49.8	48.9	47.7	46.9
97:3	50.7	50.3	49.8	48.9	47.7	46.2	45.1
98:2	49.9	48.9	48.5	47.3	45.8	43.3	40.0
99:1	47.7	47.3	46.5	45.1	43.3	41.2	38.1

119. Calculating the Results Obtained by Meissl and Hiller's Method.—For the calculation of the results, the following formulas and Table IV, containing the necessary factors worked out by Meissl and Hiller, are to be used:

Let Cu = weight of copper obtained;

P = polarization of sample (obtained as described in Art. **113**);

W = weight of sample in the 50 cubic centimeters of the solution used in Meissl and Hiller's determination;

F = factor obtained from Table IV;

$\frac{Cu}{2}$ = approximate absolute weight of invert sugar = Z;

$Z \times \frac{100}{W}$ = approximate per cent. of invert sugar = y;

$\frac{100\,P}{P+y}$ = R = relative number for cane sugar;

$100 - R$ = I = relative number for invert sugar;

$\frac{Cu\,F}{W}$ = per cent. of invert sugar. (3)

Z indicates the vertical column, and the ratio of R to I, the horizontal column of Table IV, which are used to find the factor F for calculating copper to invert sugar.

EXAMPLE.—The polarization of a sugar is 86.4, and 3.256 grams of it (W) are equivalent to .290 gram of copper. What is thè percentage of invert sugar?

SOLUTION.—

$$\frac{Cu}{2} = \frac{.290}{2} = .145 = Z$$

$$Z \times \frac{100}{W} = .145 \times \frac{100}{3.256} = 4.45 = y$$

$$\frac{100\,P}{P+y} = \frac{8{,}640}{86.4+4.45} = 95.1 = R$$

$$100 - R = 100 - 95.1 = 4.9 = I$$

$$R : I = 95.1 : 4.9$$

By consulting the table, it will be seen that the vertical column headed $I = 150$ is nearest to Z, 145, the horizontal column headed 95 : 5 is nearest to the ratio of $R : I$ (95.1 : 4.9). Where these columns meet, we find the factor 51.2 which enters into the final calculation

$$\frac{Cu\,F}{W} = \frac{.29 \times 51.2}{3.256} = 4.56,$$ the true percentage of invert sugar present. Ans.

EXAMPLES FOR PRACTICE

120. Solve the following examples:

1. A sample of raw sugar polarizes, before inversion, + 94°; after inversion, at 21° it polarizes −23°. What is the percentage of cane sugar in the sample? Ans. 88.529 per cent.

2. Another sample polarizes, before inversion, + 97°; after inversion, − 19°; the temperature at the latter observation was 21.5°. What is the percentage of cane sugar in the sample? Ans. 87.938+ per cent.

3. A sample of molasses contains 93 per cent. of cane sugar; its analysis by Meissl and Hiller's method gave .35 gram of copper and 4.3 grams of molasses had been used in this last estimation. What is the percentage of invert sugar in the sample? Ans. 4.167 per cent.

4. A sample of raw sugar polarizes, before inversion, + 96°; after inversion, − 20° at 18°. For Meissl and Hiller's determination 4 grams were used and .36 gram of copper has been obtained. What percentage of cane sugar and invert sugar is contained in this sample?

Ans. { 86.787 per cent. cane sugar
4.689 per cent. invert sugar

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121. Water and Ash Determination.—Water and ash are determined in the manner previously described. Sugar, water, and ash added together and deducted from 100 yields the non-saccharine organic matter.

122. Alkalinity.—What has been stated in Art. **103** applies also in this case. When molasses is used, 15 to 20 grams are dissolved and diluted to 250 cubic centimeters; 25 to 30 cubic centimeters of this solution are placed in a graduated cylinder and 1 to 2 cubic centimeters of litmus tincture are added. If the cylinder is held horizontally over a white piece of paper, a grayish-green color is observed in the liquid when the molasses is alkaline. In this case, another portion is titrated with standard acid, as in the method already mentioned.

To distinguish whether a molasses is neutral, the contents of the cylinder are divided into two parts. To one part, 1 drop of normal acid is added; to the other, add 1 drop of normal alkali, whereupon the solutions, if originally neutral, should become either red or blue.

123. Rendement or Yield.—Rendement or yield is the number that designates how much crystallized cane sugar is capable of being obtained from a raw sugar. The customary calculation in practice fundamentally assumes 5 parts by weight; sugar is prevented from crystallizing by 1 part by weight of soluble salts. The rendement is therefore obtained by deducting 5 times the weight of salt content from the cane-sugar content. The assumption is rather an arbitrary one.

QUANTITATIVE ANALYSIS

(PART 9)

ANALYSIS OF ASPHALT AND ASPHALTIC SUBSTANCES

1. Under this heading may be understood natural bitumens, varying in physical properties from hard, resonant, vitreous matter to soft, sticky masses. The former are known under the technical name of **asphalt,** and the latter under the name of **maltha.** With more or less mineral matter, which, likewise, can vary in physical and chemical composition, they belong to the product that, when admixed with suitable constituents and subjected to various processes, forms the basis of artificial paving. Little is known regarding the origin of these substances and the nature of their organic constituents.

2. A general description of analysis will be given. The analysis includes the estimation of water, substances soluble in petroleum ether, or *petrolene*, substances soluble in carbon disulphide or turpentine, called *asphaltene*, organic matter not bitumen, and mineral matter.

ANALYTICAL PROCESSES

3. Water.—Of the substance, 2 to 5 grams are divided as finely as possible or spread over as large a layer as possible and dried over sulphuric acid in a desiccator. The substance is reweighed and the remaining results are based on anhydrous material.

81—25

4. Petrolene.—On a weighed filter are weighed 2 to 5 grams of substance. The filter must be fitted into a much larger funnel, provided with a stop-cock on its exit tube. The contents are repeatedly washed with petroleum ether every few minutes. To remove the last traces, digest for several hours. The filter and contents are dried in a steam bath and weighed. The loss in weight represents *petrolene.*

5. Asphaltene.—The filter and contents of the previous examination are replaced on the funnel and extracted in a similar manner with turpentine. After complete exhaustion, which, at times, is tedious, the contents are washed with alcohol, dried, and weighed as before. The difference represents *asphaltene soluble in turpentine.*

The process is repeated, using chloroform for extraction. The difference represents *asphaltene soluble in chloroform.*

The three fractions are summed up as *total bitumen.*

6. Mineral Matter.—The residue is ignited in a platinum dish, cooled, and weighed. In case carbonates are present, the ash must be recarbonated by ignition with ammonium carbonate.

Matter not bitumen is that which remains when the sum of the percentages of the four previous determinations are deducted from 100.

ANALYSIS OF FATS, WAXES, AND MINERAL OILS

INTRODUCTORY

7. Fats are mixtures of triglycerides of monobasic fatty acids. Vegetable and animal waxes are fatty-acid esters of higher fatty alcohols. Mineral waxes and mineral oils consist of hydrocarbons.

The groups named, representing different chemical constitutions, show characteristic behavior toward alkalies. Fats

are saponified on treatment with alkali into salts of fatty acids (soaps) and glycerine, both of which are soluble in water. Fats, therefore, are *completely saponifiable*. Vegetable and animal waxes yield salts of fatty acids soluble in water and insoluble in higher fatty alcohols by this treatment, and are termed *incompletely saponifiable*. Mineral waxes and oils are not changed by alkalies; they are unsaponifiable.

FATS

GENERAL METHODS OF INVESTIGATION

8. Although the fats represent mixtures of many triglycerides, the quantity of the same in every kind of fat is a fairly constant one. In consequence of these so called constants, slightly varying values can be determined for each fat. These would lead with certainty to the identification of the same. Of these constants, there will be described:

1. *The Saponification Number.*—This indicates how many milligrams of potassium hydrate are necessary to saponify 1 gram of fat, and is, therefore, a representation of the capacity of saturation of the fatty acid contained in the fat.

2. *Hübl's Iodine Number.*—This represents the quantity of iodine that fat is capable of absorbing, and serves as a measure for the unsaturated acid present (oleic and linoleic acids and linoleic-acid series).

3. *The Acetyl Number.*—This is a measure of the fatty hydroxyacids and fatty alcohols present.

4. *The Acid Number.*—This expresses the number of milligrams of potassium hydrate used to neutralize the free fatty acids in 1 gram of fat. It serves, therefore, as a measure for the free acids of the fat.

SAPONIFICATION NUMBER

9. Köttstorfer's Number.—The necessary reagents to determine the saponification number are: (*a*) About a half-normal hydrochloric-acid solution, the exact value of

which has been determined by titrating with potassium hydrate. (*b*) An alcoholic solution of potassium hydrate, prepared by dissolving in a little water 30 grams of potassium hydrate in sticks, purified by alcohol, and then diluting to 1 liter with alcohol free from fusel oil. The solution is allowed to stand for 24 hours and is then filtered into a flask. A 25-cubic-centimeter pipette, provided above with a piece of rubber tubing and a clip, is inserted into the single perforation of a tight-fitting rubber stopper. When pure alcohol is used, the solution will, at the utmost, assume a slightly pale-yellow tint on standing; otherwise, it will soon assume a brown color, and must not be employed.

To conduct the operation, 1 to 2 grams of the substance are placed in a wide-necked flask of about 150 to 200 cubic centimeters capacity. For the purpose of weighing, a small bottle with a lip is preferable. Introduce 50 to 60 drops of oil from the weighing bottle into the flask and reweigh the bottle; 25 cubic centimeters of the alcoholic-potash solution are introduced into the flask by means of the pipette before mentioned. An upright condenser is fitted into the flask and the whole heated to boiling on a water bath, and shaken from time to time. Saponification is, as a rule, complete in 15 minutes; but, with difficultly saponifiable fats, $\frac{1}{2}$ hour is occasionally required. A few drops of phenol-phthalein solution are then added and the excess of alkali titrated with the half-normal hydrochloric-acid solution.

Since the standard of the alcoholic potash alters somewhat, 25 cubic centimeters of it are titrated anew with the hydrochloric acid prior to each experiment. The same conditions as heretofore are to be observed, namely, the same period of heating on the water bath and the same degree of heat. The difference between the number of cubic centimeters of hydrochloric acid used in this and the previous titration is expressed in milligrams KOH and calculated to 1 gram fat to obtain the saponification number.

IODINE NUMBER

10. Hübl's Iodine Number.—The determination of the iodine absorption of oils and fats is probably the most important test. Although iodine acts only slowly on fats, unsaturated fatty acids readily form chloriodine addition products on treatment with an alcoholic solution of iodine and mercuric chloride. The reagents required are as follows:

1. *Iodine Solution.*—Pure iodine to the amount of 25 grams is dissolved in 500 cubic centimeters of 95-per-cent. alcohol free from fusel oil, and 30 grams of mercuric chloride in the same volume of alcohol. The latter solution, if necessary, is filtered, and then the two solutions mixed. The mixed solution should be allowed to stand at least 12 hours before using.

2. *Decinormal Sadium-Thiosulphate Solution.*—This is prepared by dissolving 24.6 grams of chemically pure sodium thiosulphate, freshly pulverized as finely as possible and dried between filter paper, in water, and making up the solution to 1 liter.

3. *Starch Paste.*—For 10 minutes, 1 gram of starch is boiled in 200 cubic centimeters of distilled water, and cooled to room temperature.

4. *Solution of Potassium Iodide.*—Potassium iodide to the amount of 150 grams is dissolved in water, and the solution made up to 1 liter.

5. *Solution of Potassium Bichromate.*—Chemically pure potassium bichromate to the amount of 3.874 grams is dissolved in distilled water, and the volume made up to 1 liter.

11. Standardizing the Sodium-Thiosulphate Solution.—Place 20 cubic centimeters of the potassium-bichromate solution, to which has been added 10 cubic centimeters of the solution of potassium iodide, in a glass-stoppered flask. Add to this mixture 5 cubic centimeters of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask from a burette until the liquid becomes nearly colorless. Add then a few drops of

starch solution, and, with constant shaking, continue to add sodium thiosulphate until the blue color just disappears. The number of cubic centimeters of thiosulphate solution used, multiplied by 5, is equivalent to 1 gram of iodine.

For example, 20 cubic centimeters of potassium-bichromate solution required 16.2 cubic centimeters of sodium thiosulphate; then $16.2 \times 5 = 81$ = number of cubic centimeters of thiosulphate solution equivalent to 1 gram of iodine. Then, 1 cubic centimeter of sodium thiosulphate = .0124 gram of iodine.

12. Actual Determination of Iodine Number. From .15 to .18 gram of drying oils, .25 to .30 gram of non-drying oils, or .8 to 1 gram of solid fats, is weighed into a glass-stoppered bottle of 300 cubic centimeters capacity. To this is added 10 cubic centimeters of chloroform, and, after solution has taken place, 30 cubic centimeters of the iodine solution are added. The flask is then set aside in a dark place and allowed to stand, with occasional shaking, for at least 3 hours.

To the contents of the flask, 100 cubic centimeters of distilled water are added, together with 20 cubic centimeters of the potassium-iodide solution. Any iodine that may be noticed on the stopper of the flask should be carefully washed back into the flask with the potassium-iodide solution. The excess of iodine is now taken up with the sodium-thiosulphate solution, which is run in gradually from a burette, with constant shaking, until the color of the solution has almost disappeared. A few drops of starch paste are then added, and the titration continued until the blue color, produced by the addition of the latter, has entirely disappeared. Toward the end of the reaction, the flask should be stoppered and violently shaken, so that any iodine remaining in solution in the chloroform may be taken up by the potassium-iodide solution in water. A sufficient quantity of sodium-thiosulphate solution should be added to prevent the reappearance of any blue color in the flask for 5 minutes.

TABLE I

Fats	Iodine Number			Saponification Number		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean
Olive oil	79	88	82–83	185	196	193
Sesame oil	103	112	108–109	187	192	190
Peanut oil	87.3	103	94–96	190	197	194
Cotton oil	102	112	108–109	191	198	195.5
Castor oil	82	85.9	84.5	176	183	180
Rape-seed oil	98	104	100–101	175	179	177
Linseed oil	170	183	178	187.4	195.2	192
Hemp-seed oil	140.5	157.5	150	190	193	191.5
Sunflower-seed oil	122	134	128	189	194	192
Cod-liver oil	123	166	144–148	175	194	182–187
Palm oil	51	52.4	51.5	200	202.5	201.5
Cocoanut oil	8	9.35	8.5	253	262	257
Butter fat	26	35	33	221	227	224
Tallow	35.5	44	39	193	206	197
Bone fat	46	55	49	....	....	190.9

At the time of adding the iodine solution to the oils or fats, two flasks of the same size as that used for the determination should be employed for conducting the operation described above, but without the addition of the oils or fat. In every respect, the performance of the blank experiments should be just as described. The blank determinations must be made each time the iodine solution is used; for example:

Blank Determinations

(1) 30 c. c. of iodine solution required 46.4 c. c. of sodium-thiosulphate solution.

(2) 30 c. c. of iodine solution required 46.8 c. c. of sodium-thiosulphate solution.

Mean equals 46.6 c. c.

Per cent. of iodine absorbed:

Weight of oil taken........................	1.0479 gr.
Quantity of iodine solution used.............	30 c. c.
Thiosulphate equivalent to iodine used......	46.6 c. c.
Thiosulphate equivalent to remaining iodine.	14.7 c. c.
Thiosulphate equivalent to iodine absorbed..	31.9 c. c.

Per cent. of iodine absorbed, $31.9 \times .0124 \times 100 \div 1.0479 = 37.75$, which would be the *iodine number* for the oil under examination.

Table I contains the iodine numbers and saponification numbers of the most important fats. The maximum and minimum values shown in the table are rarely found. Normal values are those under the heading "Mean."

ACETYL NUMBER

13. The acetyl number of Ulzer and Benedict expresses the number of milligrams of potassium hydrate that is necessary to saponify the acetyl groups in 1 gram of acetylized fat.

To determine this, the free fatty acids must first be isolated from the fats, for which purpose 30 grams of fat are placed in a flask with 60 to 70 cubic centimeters of alcohol and 10 grams potassium hydrate, dissolved in a little water. This is boiled on a water bath with an upright condenser to complete saponification. The latter is finished when, after addition of some water and shaking, the liquid remains perfectly clear. The excess of alcohol is evaporated on the water bath. The remaining soap is dissolved in warm water and is poured into a beaker of 1,000 cubic centimeters capacity. The solution is boiled with dilute sulphuric acid until the fats are completely melted. A current of carbonic-acid gas is, at the same time, run through the solution to prevent bumping. Thereupon the acid fluid is siphoned off and the fats are again boiled with water. The acid liquor is again siphoned off, and the operation is repeated until the liquid siphoned off no longer reacts acid. The acids are filtered on a hot-water funnel through a dry filter and are

acetylized by boiling for 2 hours with an equal volume of acetic anhydride in a flask provided with an upright condenser. The contents of the flask are poured into a beaker of 1,000 cubic centimeters capacity, mixed with 500 to 600 cubic centimeters of water and boiled for ½ hour. As before, carbonic-acid gas is conducted through a tube extending nearly to the bottom of the beaker. After the expiration of the time mentioned, the water is siphoned off, and the boiling with fresh portions of water is repeated three times, whereby all acetic acid is removed. Finally, the acetylized acids are filtered in an air bath at about 80° through a dry filter. In a portion of the acetylized acids, the saponification number is determined, as has been described in the preceding articles. This gives the *acetyl saponification number.* In another portion, the *acetyl acid number* is determined as described in Art. **14,** in the method for acid number. The difference between the two gives the *acetyl number.* If a fat contains no fatty hydroxyacids, its accetyl number will equal zero.

ACID NUMBER

14. Determination of Acid Number.—Acidity in oil is generally due to partial decomposition of the oil with liberation of fatty acids. These latter act as corrosive agents, attacking the metal bearings of machinery, forming metallic soaps and producing gumming and thickening of the lubricant.

Properly refined mineral oils are free from acidity, but nearly all animal and vegetable oils possess it more or less. In palm oil, for instance, the free fatty acids vary from 12 to 80 per cent., and, in olive oil, from 2.2 to 25.1 per cent. of free acid (oleic) has been found.

Oleic acid cannot, of course, be present as a constituent of a pure mineral oil; still the acid test should be made, since poorly refined mineral oils are liable to contain small amounts of sulphuric acid left in the process of refining.

About 10 grams of the substance under examination are slightly heated in a flask with about 50 cubic centimeters of

pure, acid-free, 95-per-cent. alcohol, while the liquid is agitated. On cooling, phenol phthalein is added, and the solution titrated with half-normal alkali until the red color appears. The number of milligrams of potassium hydrate required, calculated to 1 gram of the substance, yields the acid number. When free fatty acids are used, the acid number is identical with the saponification number.

Frequently, the acid number of a substance is expressed in *Burstyn degrees*. These express the number of cubic centimeters of normal alkali necessary to combine with the free acids present in 100 cubic centimeters of the substance.

COLOR REACTIONS OF OILS

15. Many fatty oils, when treated with chemical reagents, very often produce strongly colored products. To a certain extent, these color reactions are characteristic of the oils by which they are produced, and, hence, may be employed for their identification. It must be remembered, however, that the albuminous, resinous, and other foreign matters, on the presence of which the color reactions in most cases depend, are more or less completely removed or modified by the process employed for refining oil. Hence, considerable variations are observed in the behavior of different samples of oil with the same reagent, and the value of the reactions is still further reduced by the modifications produced by the presence of free fatty acids in the oils. Still less are the indications to be trusted when mixed oils are examined. Notwithstanding these drawbacks, color tests, when carefully applied, are often capable of furnishing valuable information, and sometimes render the positive identification of an oil, or its detection in a mixture, possible, when no other means are available.

The reactions with strong sulphuric and nitric acids are the most valuable; it is advisable, in employing color tests, to examine specimens of oils of known purity side by side with the sample, instead of trusting too implicitly the reactions described.

TABLE II

COLOR REACTIONS OF VEGETABLE OILS

Name of Oil	1 or 2 Drops of Strong Sulphuric Acid to 20 of Oil	
	Before Stirring	After Stirring
Olive oil	Yellow, green, or pale brown.	Light brown, or olive green.
Almond oil	Colorless, or yellow.	Dark yellow, olive, or brown.
Arachis oil	Grayish yellow to orange.	Greenish, or reddish brown.
Rape-seed oil, crude	Green with brown rings	Bright green, turning brownish.
Rape-seed oil, refined	Yellow, with red or brown rings.	Brown.
Mustard oil	Dark yellow, with orange streaks.	Reddish brown.
Cottonseed oil, crude	Very bright red.	Dark red, nearly black.
Cottonseed oil, refined	Reddish brown.	Dark reddish brown.
Niger-seed oil	Yellow, with brown clot	Reddish or greenish brown.
Poppy-seed oil	Yellow spot, with orange streaks or rings.	Olive or reddish brown.
Linseed oil, raw	Hard brown or greenish brown clot.	Mottled, dark brown.
Linseed oil, boiled	Hard brown clot.	Mottled, dark brown.
Castor oil	Yellow to pale brown.	Nearly colorless, or pale brown.

COLOR REACTIONS OF ANIMAL OILS

Lard oil............	Greenish yellow, or brownish with brown streaks.	Mottled or dirty brown.
Tallow oil..........	Yellow spot, with pink streaks.	Orange red.
Whale oil	Red, turning violet.	Brownish red, turning brown or black.
Seal oil.............	Orange spot, with purple streaks.	Bright red, changing to mottled brown.
Cod-liver oil........	Dark red spot, with purple streaks.	Purple, changing to dark brown.
Sperm oil	Pure brown spot, with faint yellow ring.	Purple, changing to reddish or dark brown.

COLOR REACTIONS OF HYDROCARBON OILS

Petroleum lubricating oil...........	Brown.	Dark brown, with blue fluorescence.
Shale lubricating oil	Dark reddish brown.	Reddish brown, with blue fluorescence.
Rosin oil, brown....	Bright mahogany brown.	Dark brown, with purple fluorescence.
Rosin oil, pale......	Mahogany brown.	Red brown, with purple fluorescence.

16. Sulphuric-Acid Color Test.—Of color tests, that with concentrate sulphuric acid is one of the most valuable and readily applied. Table II shows the effect produced on placing a drop or two of sulphuric acid in the center of about 20 drops of the oil, and observing the color both before and after stirring. The reactions described include those produced by the majority of hydrocarbon oils. As already stated, the colors produced by different samples of the same kind of oil are liable to considerable variation.

The reactions of oils with concentrate sulphuric acid are sometimes complicated or rendered indistinct by the charring action exerted by the reagent. This may be avoided by dissolving 1 drop of the oil in 20 drops of carbon disulphide, and agitating the solution with a drop of sulphuric acid. Whale oil, thus treated, gives a fine violet coloration, quickly changing to brown; whereas, with sulphuric acid alone, a mere red or reddish-brown color changing to brown or black is obtained.

17. Nitric-Acid Color Test.—The color reactions of oils with nitric acid are sometimes characteristic, especially in the case of seed oils. The test is recommended to be applied in various ways, but perhaps those methods that combine observations of the color and the character of the elaidin are to be preferred. Thus, O. Bach agitates 5 cubic centimeters of the sample with an equal volume of nitric acid, Sp. Gr. 1.30. After noting any coloration, the mixture is immersed in boiling water for 5 minutes and the effect again observed. A more or less violent reaction often occurs on heating, even resulting, as in the case of cotton or sesame oils, in the mixture being projected from the tube. The results of this method, obtained by Bach, are given in Table III.

TABLE III

Oil	After Agitation With Nitric Acid	After Heating For 5 Minutes	After Standing 12 to 18 Hours
Olive oil	Pale green	Orange yellow	Solid
Arachis oil ...	Pale rose	Brownish yellow	Solid
Rape-seed oil.	Pale rose	Orange yellow	Solid
Sesame oil....	White	Brownish yellow	Liquid
Sunflower oil.	Dirty white	Reddish yellow	Buttery
Cottonseed oil	Yellowish brown	Reddish brown	Buttery
Castor oil	Pale rose	Golden yellow	Buttery

A similar test has been described by Massie, who agitates 10 grams of the oil with 5 cubic centimeters of nitric acid, Sp. Gr. 1.40, and 1 gram of mercury, and observes the color

of the product after 1 hour, and also the time required for solidification. The results thus obtained are given in Table IV.

TABLE IV

Oil	Coloration	Minutes for Solidification
Olive oil.............	Pale yellowish green	60
Hazelnut oil..........	White	60
Almond oil...........	White	90
Arachis oil...........	Pale reddish	105
Apricot oil...........	Rose	105
Rape-seed oil.........	Orange	200
Cottonseed oil........	Orange red	105
Sesame oil...........	Yellowish orange	150
Beechnut oil.........	Reddish orange	360
Poppy-seed oil........	Red	Fluid

18. Nitric and Sulphuric Acid Color Test.—A mixture of strong sulphuric and nitric acids, used in the proportion of 1 drop to 10 drops of the oil, has been proposed by H. Meyer as a color test for certain fish oils. The following reactions were obtained with this test:

TABLE V

Oil	Sp. Gr. of Sample	Before Stirring	After Stirring
Cod-liver oil..	.9290	Violet, quickly becoming rose red.	Rose red, changing to light brown.
Hake-liver oil.	.9270	Dark violet, changing to dark brown.	Brownish violet, changing to light brown.
Skate-liver oil.	.9327	Light violet, changing to brown.	Brownish violet, changing to brown.
Shark-liver oil	.9285	Light brown, with spots of red.	Light brown, becoming darker.
Herring oil...	.9326	Brown.	Dark brown.
Sprat oil......	.9284	Light brown.	Unchanged.
Seal oil.......	.9245	Light brown.	Lemon yellow, changing to emerald green and bluish green.
Whale oil.....	.9301	Light brown.	Darker.

CLASSIFICATION OF FATS

19. Fats may be divided into two classes, viz., **liquid fats** and **solid fats.** The former are again subdivided into four subsidiary classes, viz., *drying oils*, *non-drying oils*, *fish oils*, and *fluid waxes.*

LIQUID FATS

20. Drying Oils.—Many oils thicken on exposure to air, and, under favorable circumstances, gradually dry up into yellowish, transparent varnishes or resins, thereby absorbing considerable oxygen; they mainly consist of glycerides of linoleic acid, but they do not yield elaidin. Oils that possess this property are termed **drying oils.**

21. Non-Drying Oils.—These oils contain much olein, and dry with the utmost difficulty in the air or at higher temperatures. They absorb only small quantities of oxygen, but form elaidin.

22. Fish Oils.—**Fish oils** are obtained from the fat of fish; they absorb considerable quantities of oxygen, but do not dry up to a varnish on exposure to air, and yield little or no elaidin. They give intense colorations with caustic soda, sulphuric acid, nitric acid, and phosphoric acid, of which that obtained with the latter acid serves conditionally to distinguish them from other oils. It is obtained by warming 5 volumes of oil with 1 volume of glacial phosphoric acid. By this treatment, all fish oils, whether mixed or not, give an intense red, brown-red, or brown-black shade.

23. Fluid Waxes.—**Fluid waxes** obtained from the oil of marine animals consist mainly of esters of monatomic alcohols, and contain only a small amount of glycerides. They are, like true waxes, only partially saponifiable, and possess, in consequence, a very low saponification number. The unsaponified portion is solid and consists of monatomic alcohols. They contain only 60 to 65 per cent. fatty acids, as against 95 per cent. in other oils. They absorb very little

oxygen when exposed to air, do not dry to a varnish, and give no elaidin.

24. Recognition of Drying and Non-Drying Oils. For testing drying properties of oil, a definite number of drops of the sample may be placed in a watch glass and exposed to a temperature of about 100° for from 12 to 24 hours, side by side with samples of oil of known purity. Olive oil will scarcely be affected by such treatment, and rape oil will only thicken somewhat. Cottonseed oil will be considerably affected, while good linseed oil will form a hard skin or varnish, that can only be ruptured with difficulty by pressure with the finger. In some respects, a preferable plan is to flood a thin piece of glass with the oil. The glass with the adhering film of oil is then kept at 100° and the progress of drying watched by touching, at intervals, successive parts of the plate with the finger.

These methods require, however, a great deal of time, and the determinations hardly furnish a sure means of recognition, so that the elaidin reaction is preferable in any case.

25. Elaidin Reaction.—When oleic acid is treated with a few bubbles of nitrogen trioxide, it is gradually changed into the isomeric body, elaidic acid, which is solid at ordinary temperatures. Olein undergoes a similar change with production of the solid isomeric elaidin, as also do such oils as consist of olein in a state of approximate purity. On the contrary, the drying oils, which consist chiefly of the glycerides of linoleic acids, are not visibly affected by treatment with nitrous acid. Oils that probably consist of mixtures of olein with more or less linolein give less solid products with nitrous acid than the approximately pure oleins.

The following method of obtaining the elaidin reaction, due to Poutet, has been studied by Archbutt, and is undoubtedly one of the best.

Mercury to the amount of 1 cubic centimeter should be dissolved in 12 cubic centimeters of cold nitric acid of 1.42

Sp. Gr.; 2 cubic centimeters of the freshly made, dark-green solution is then shaken into a wide-mouthed stoppered bottle with 50 cubic centimeters of the oil to be tested, and the shaking repeated every 10 minutes during 2 hours. When treated in this manner, oils consisting of approximately pure olein, or of mixtures of olein with the solid esters, such as palmitin and stearin, give a solid product of greater or less consistency. Olive oil is remarkable for the canary, or lemon-yellow, color and great firmness of the elaidin yielded by it. After 24 hours, the hardness of the product is such that it is impervious to a glass rod, and sometimes rings when struck with it, but this characteristic is also possessed by the elaidins yielded by arachis and lard oils. In making the elaidin test, it is important to note the time required to obtain a solid product that will not move on shaking the bottle, as well as the time required for its ultimate consistency. Also, the temperature should be kept as nearly constant as possible, or erratic results may be obtained, and comparison of different oils becomes impossible.

The behavior of the various more important liquid fats is as follows: A hard mass is yielded by olive, almond, lard, sperm, and sometimes neat's-foot and arachis oils. A product of the consistency of butter is given by neat's-foot, mustard, and sometimes by arachis, sperm, and rape oils. A pasty or buttery mass that separates from a fluid portion is yielded by rape, sesame, cottonseed, sunflower, niger-seed, cod-liver, seal, whale, or porpoise oil. Liquid products are yielded by linseed, hemp-seed, walnut, and other drying oils.

26. Maumené's Test.—This test depends on the phenomenon that sulphuric acid, mixed with drying oils, heats up considerably more than with the non-drying oils. The following method of performing Maumené's test is that recommended by Archbutt and has been successfully employed by the writer:

Into a beaker of 200 cubic centimeters capacity is weighed 50 grams of the oil under examination, and the beaker immersed in a capacious vessel of water, together with a

bottle of strong sulphuric acid, until they are both at the same temperature, which should not be far from 20°. The beaker containing the oil is then wiped, and placed in a cotton-wool nest previously made for it in a cardboard box or wide beaker. The immersed thermometer is then observed, and the temperature recorded; 10 cubic centimeters of the concentrate sulphuric acid should then be withdrawn from the bottle with a pipette, and allowed to run into the oil. During the addition of the acid, which should occupy about 1 minute, the mixture must be constantly stirred with the thermometer, and the agitation continued until no further rise of temperature ensues. This point is readily observed, as the indication remains constant for 1 or 2 minutes, and the temperature then begins to fall. Should the rise equal more than 70°, drying oils or fish oils can be considered present with certainty. As an example, olive oil shows a rise of 41° to 43° in temperature, rape oil 51° to 60°, and linseed oil 104° to 111°.

27. Iodine Number.—The non-drying oils possess lower iodine numbers than the drying oils. The iodine number, in consequence, serves as a convenient and safe means of identification, provided that fish oils are absent. These are non-drying, and yet possess a high iodine number.

SOLID FATS

28. The recognition of the solid fats is accomplished chiefly by the (*a*) determination of specific gravity; (*b*) determination of melting and solidification points; (*c*) behavior in the refractometer; (*d*) determination of saponification and iodine numbers; (*e*) determination of volatile fatty acids by the Reichert-Meissl number.

29. Specific Gravity.—The specific gravity may be conveniently determined by the method of Gintl, who uses a small cylindrical flat-bottomed flask, the opening of which may be closed with a ground-glass plate. When filling in

the molten fat, an excess is allowed to remain above the top. After cooling, the plate is slipped on and screwed down. The excess is wiped off with a cloth dipped in petroleum ether. The weight of an empty flask, a flask filled with water at 15.5°, and a flask filled with the cooled fat are determined in the usual manner, and the specific gravity of the fat is obtained by dividing its weight by that of the water. For example:

Weight of flask, dry..........	10.0197 grams
Weight of flask, plus water....	37.3412 grams
Weight of water..............	27.3215 grams
Weight of flask, plus fat......	34.6111 grams
Weight of fat................	24.5914 grams

Specific gravity = 24.5914 ÷ 27.3215 = .90008

According to the method of Hager for the determination of specific gravity, the molten fat is drawn up into a pipette, from which it is allowed to drop slowly from the height of 1 inch into a glass dish filled with 60 to 90 per cent. of alcohol. The solidified drops are placed in the liquids, which serve to determine specific gravity. For densities less than water, a mixture of water and alcohol is used; and, for greater densities, a mixture of glycerine and water or alcohol is used. Glycerine or glycerine and water are added until the drop just floats on the liquid, which is set in rotation. Finally, the liquid is poured through glass wool, and the specific gravity, which is equal to that of the fat, is then determined by means of a hydrometer or pycnometer.

The great objection to this otherwise very ingenious method is that fat and waxes that have undergone sudden cooling have, very often, abnormal specific gravities; hence, the results cannot be too strictly relied on.

30. Melting and Solidification Points.—Full directions for the determination of the melting and solidification points will be given in the discussion of tallow and waxes.

31. Behavior in the Refractometer.—Valuable indications as to the identity and purity of fats and oils,

especially butter fat, may be gained from the determination of the refractive index. This may be done by means of Abbé's refractometer, shown in Fig. 1, observing the total

Fig. 1

reflection that a thin stratum of the fat or oil placed between prisms of a more highly refractive substance produces in transmitting light. The following description of the method of using the instrument is taken from the bulletin of the Association of Official Agricultural Chemists.

A piece of fine tissue paper, 3 centimeters in length by 1.5 centimeters in width, is placed on the lower of the two prisms of the apparatus (not shown in the figure). On this paper are placed 2 or 3 drops of the fat or oil, and the upper prism is carefully fixed in position, so as not to move the paper from its place. In charging the apparatus with the oil in this way, it is placed in a horizontal position. After the paper holding the fatty substance is secured by replacing the upper prism, the apparatus is placed in its normal position

and the index moved until the light directed through the apparatus by the mirror shows the field of vision divided into dark and light portions. The dispersion apparatus *a* is now turned until the rainbow colors on the part between the dark and light fields have disappeared. Before doing this, however, the telescope *b* (the eyepiece of the apparatus) is so adjusted as to bring the cross-lines of the field of vision distinctly into focus. The index *c* of the apparatus is now moved back and forth until the line of the two fields of vision falls exactly at the intersection of the cross-lines. The refractive index of the fat under examination is then read directly on the scale *d* by means of a small magnifying glass. To check the accuracy of the first reading, the dispersion apparatus is turned through an angle of 180° until the colors have again disappeared, and, after adjustment, the scale of the instrument again read. These two readings should nearly coincide, and their mean is the true reading of the fat under examination.

For butter fats, the apparatus should be kept in a warm place, the temperature of which does not fall below 30°. For reducing the results obtained to a standard temperature, say 25°, the factor .000176 should be employed. As the temperature rises the refractive index falls. For example:

Refractive index of a butter fat determined at 32.4° = 1.4540, reduced to 25° as follows: $32.4-25 = 7.4$; $.000176 \times 7.4 = .0013$; then, $1.4540+.0013 = 1.4553$.

The instrument used should be set with distilled water at 25°, the theoretical refractive index of water at that temperature being 1.333. In the determination given in the example, the refractive index of pure water measured 1.3300; hence, the given number should be corrected by the addition of .0030, making the corrected index of the butter fat mentioned, at the temperature given, 1.4583.

32. The following numbers in Table VI show the refractive indexes for some of the more common oils, that of water being taken as 1.333 at 25°.

TABLE VI

Name	Temperature	Refractive Index	Calculated for 25°
Olive oil (France)	26.6°	1.4673	1.4677
Olive oil (California).....	25.4°	1.4677	1.4678
Cottonseed oil...........	24.8°	1.4722	1.4721
Cottonseed oil...........	26.3°	1.4703	1.4709
Cottonseed oil...........	25.3°	1.4718	1.4719
Sesame oil..............	24.8°	1.4728	1.4728
Sesame oil..............	26.8°	1.4710	1.4716
Castor oil...............	25.4°	1.4771	1.4773
Lard oil	27.3°	1.4657	1.4666
Peanut oil	25.3°	1.4696	1.4696

33. Volatile Fatty Acids.—A useful method of examining fats and oils consists in determining the amount of alkali required to neutralize the volatile fatty acids. These are determined by the Reichert-Meissl number, which represents the number of cubic centimeters of one-tenth normal alkali that is necessary to neutralize the volatile fatty acids in 5 grams of fat.

About 5 grams of fat are placed in a 200 to 300 cubic-centimeter flask on a water bath to which about 2 grams of potassium hydrate in sticks, chemically pure by alcohol, and 50 cubic centimeters of 70 per cent. of alcohol are added, and the whole saponified, shaking the flask at frequent intervals. After complete saponification, the heat is increased and the alcohol volatilized until a thick soap only remains in the flask. This is dissolved by heating gently with 100 cubic centimeters of water; 40 cubic centimeters of dilute sulphuric acid (1 : 10) and a few pieces of pumice stone are added and the flask connected, by means of a bulb tube, with a Liebig condenser. It is first heated with a small flame until the fats have melted to a clear layer, after which it is distilled and exactly 110 cubic centimeters of the distillate

are collected in a flask graduated thus. The time of distillation should be so regulated that it does not occupy less than 30 minutes. After thoroughly shaking up the contents of the flask, 100 cubic centimeters are filtered off into a measuring flask or cylinder, transferred to a beaker of appropriate size, and titrated with $\frac{n}{10}$ alkali, using phenol-phthalein as an indicator. The quantity of alkali used is increased one-tenth and calculated on exactly 5 grams of fat.

The Reichert-Meissl method is very frequently used to identify butter and cocoanut oils. Butter has a number ranging from 26 to 29; cocoanut oil, 7.

34. Detection of Hydrocarbon Oils.—The extensive and cheap production of various hydrocarbon oils suitable for lubricating purposes has resulted in their being largely employed for the adulteration of animal and vegetable oils. The hydrocarbons most commonly employed are:

1. Those produced from petroleum and by distillation of bituminous shale.
2. Those produced by the distillation of common rosin.
3. Neutral coal oil, being the portion of the products of the distillation of coal tar, boiling above 170°.
4. Solid paraffin, employed for the adulteration of beeswax and spermaceti, and used in admixture with stearic acid for making candles.

The presence of hydrocarbons in fats and fatty oils is detected (1) by the altered density of the sample, which is decreased by members of the first class and increased by rosin and coal-tar products; (2) by the lowering of the flashing and boiling point; (3) by the fluorescence of members of the first two classes; (4) and by the incomplete saponification by alkalies. The taste and odor, on heating, are also valuable indications.

Specific gravity is a character of some little value for detecting and approximately estimating hydrocarbon, but in practice the indications obtained are apt to be rendered

valueless by the employment of a mixture that has the same density as the oil to be adulterated.

The tendency of a hydrocarbon is to reduce the flashing and boiling points of the fixed oil, and, in some cases, a distinct separation may be effected by fractional distillation.

Fluorescence is a character of considerable value for detecting the presence of hydrocarbons. If undoubtedly fluorescent, the sample certainly contains some hydrocarbon, but the converse is not strictly true, as the fluorescence of some varieties can be destroyed by treatment, and some hydrocarbons possess no fluorescence whatever. Most of the hydrocarbons employed for lubricating purposes are strongly fluorescent, and the many others become so on treatment with an equal volume of strong sulphuric acid. A hydrocarbon possessing strong fluorescence may be evident in presence of a very large proportion of fixed oil; but, if any doubt exists, the hydrocarbon should be isolated in the manner described further on.

The fluorescence may usually be seen by holding a test tube filled with the oil in a vertical position in front of a window, and looking at the sides of the test tube from above. A better method, perhaps, is to lay a glass rod, previously dipped in the oil, down on a table in front of a window, so that the oily end of the rod shall project over the end of the edge of the table, and be seen against the dark background of the floor. Another plan is to make a thick streak of the oil on a piece of black marble, or glass plate, smoked at the back, and to place the streaked surface in a horizontal position in front of, and at right angles to, a well lighted window. Examined in this manner, very slight fluorescence is readily perceptible. If at all turbid, the oil should be filtered before applying the test, as the reflection of light from minute floating particles is apt to be mistaken for true fluorescence. In some cases, it is desirable to dilute the oil with ether, to which an exceedingly small amount of mineral oil is sufficient to impart a strong blue fluorescence. This is useful in the examination of very dark oils, as the color is reduced without the intensity of the fluorescence being

correspondingly decreased. If the oil is very dark, for example, a dark Gallipolio or brown rape-seed oil, it should be first refined by agitating it successively with small proportions of concentrated sulphuric acid, water, and solution of sodium carbonate, and subsequently filtering. In some cases, decolorization may be effected by warming the oil and agitating it with freshly burnt animal charcoal, the liquid being subsequently filtered.

It must be remembered that fluorescence is not perceptible by gas light, but may be brought out by burning a piece of magnesium ribbon in the proper position.

35. Quantitative Estimation of Hydrocarbon Oils. The quantitative analysis of mixtures of fat or fatty oils with hydrocarbons is best carried out by the following method, which combines rapidity, certainty, tolerable accuracy, and general applicability, and, at the same time, furnishes the hydrocarbons in a condition for further examination.

The hydrocarbons that are to be determined are all unaffected by alkalies, whereas animal and vegetable oils and waxes undergo saponification. If potash or soda is employed, the resultant soap is soluble in water. The hydrocarbons, though insoluble in water and unaffected by alkalies, dissolve with greater or less facility in concentrated solution of soap and are very imperfectly separated on dilution. They may, however, be dissolved out from the dry soap by ether, chloroform, carbon disulphide, benzene or petroleum spirit. In some cases, a good separation is obtainable, but, in others, a considerable quantity of soap passes into solution, especially if the solvent is employed at a temperature approaching the boiling point. This tendency of the soap to undergo solution may be avoided by treating the aqueous solution with the solvent instead of the dry soap.

The following are the details of the manipulation: Of the sample 5 grams are saponified by alcoholic alkali, the solution partly freed from alcohol, and transferred to a separator of about 200 cubic centimeters capacity, shown in Fig. 2, furnished with a stop-cock *a* below and a stopper *b* at the

top. The tube below the stop-cock should be ground or filed off obliquely, so as to prevent any liquid remaining in it. The liquid is diluted with water until it measures from 70 to 100 cubic centimeters. From 50 to 60 cubic centimeters of ether should be next added, the stopper inserted, the liquids thoroughly shaken and allowed to rest for a few minutes. As a rule, two well defined layers will form, the lower one brownish, consisting of the aqueous solution of soap, the upper of ether, containing any hydrocarbon in solution. Separation does not always occur readily, the liquid remaining apparently homogeneous, or assuming a gelatinous consistency.

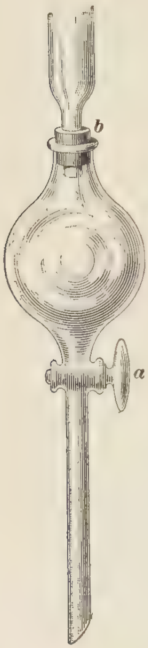

FIG. 2

In such cases, separation may be induced by thoroughly cooling the contents of the separator, by adding caustic-soda solution, by adding more ether and reagitating; or, if all these means fail, a few cubic centimeters of alcohol may be added, and a gentle rotary movement imparted to the liquid, avoiding complete admixture, when a rapid separation of the ethereal layer almost invariably occurs. The aqueous liquid is then run through the tap into a beaker. About 10 cubic centimeters of water and a few drops of caustic-alkali solution are added to the ether that remains in the separator and the whole agitated. The washings are then run off in their turn, and, after repeating the treatment with water, which is removed by the tap as before, the ethereal solution is poured off through the mouth into a weighed flask. The aqueous liquid and washings are then returned to the separator and agitated with a fresh quantity of ether, which is washed and poured into the flask as before. The agitation of the soap solution is repeated once more, when the extraction of hydrocarbon oil will be complete.

The ethereal solution will usually be strongly fluorescent. The flask containing it is attached to a condensing arrange-

ment, and the greater part of the ether distilled off by immersing the flask in boiling water. When distillation has ceased, the condenser is detached and the flask placed on top of a drying oven, by which the rest of the ether is soon dissipated. Sometimes the hydrocarbon will contain globules of water, in which case the flask should be held horizontally, and rotated rapidly, so as to spread the oil over the sides in a very thin layer and facilitate the evaporation of the water. When no more water is visible and the smell of ether is only faintly perceptible, the flask is placed on its side in the drying oven for 10 to 15 minutes and weighed, when the increase of weight over the original tare gives the amount of hydrocarbon oil extracted. Sometimes it is very difficult to obtain a constant weight by the means just indicated. In such a case, instead of heating the flask on the drying oven, it should be kept on the bath of boiling water, and a moderate current of air, filtered by passing it through a tube containing cotton wool, should be blown through it by a second tube passing through the cork. The fittings are then detached, and the flask heated for a short time in the drying oven to constant weight. Prolonged heating should be avoided, as many hydrocarbons are sensibly volatile at 100°.

EXAMINATION OF COMMON FATS

36. It is impossible, of course, in a work of this kind to lay out hard-and-fast schemes of analysis that will meet all requirements and fit for all cases, and, in the following articles, only indications and hints are given to assist the student. He will have to rely on his own judgment, assisted by what he has learned so far, as to how he must proceed in each particular case, and he will have to refer to works on analysis that treat especially on the analysis of oil, adulteration of commercial and food products, etc.

OLIVE OIL

37. Olive oil is the extraction product of the fruit of the olive. It varies somewhat in its physical properties according to quality. The finest kinds have a pale-yellow

color with a tinge of green, are almost entirely odorless, and have a mild and agreeable taste; while inferior kinds have a greenish-yellow to brownish-red color, an unpleasant odor, and a decided acrid after-taste.

Olive oil is a type of the non-drying vegetable oils; it does not thicken to any extent when exposed to air, but gradually becomes rancid, a change that seems to be dependent, to a great extent, on the presence of certain albuminous and mucilaginous matters.

Owing to the steady demand, it is very often adulterated, and cottonseed oil is perhaps the most frequent adulterant, but arachis, sesame, poppy-seed, and rape-seed oils are also occasionally employed. Fish and lard oils, however, are seldom used.

38. In the examination of olive oil, the most valuable indications are its specific gravity, the saponification equivalent, the iodine number, the rise of temperature on treatment with sulphuric acid, and the elaidin test.

The specific gravity of olive oil varies appreciably with the quality, the most acid specimen possessing the lowest density. The range of specific gravity allowed by the American Pharmacopœia is between .915 and .918 at a temperature of 15.5°. In about eighty samples of genuine, unadulterated olive oil, examined by Archbutt, the specific gravity at 15.5°, compared with water at exactly the same temperature, never exceeded .917 and was rarely as high, while the lowest specific gravity .9136 was noticed in a sample containing 24.5 per cent. of free oleic acid. Hence, in judging the character of an olive oil from its specific gravity, the quantity of free acid should always be taken into consideration. Taking the average specific gravity of genuine neutral olive oil as .917, it appears that each 5 per cent. of free acid diminishes the specific gravity of the sample by, approximately, .0007. Adulteration of olive oil with rape oil will tend slightly to reduce the specific gravity of the sample, while the addition of such oils as cottonseed, sesame,

poppy-seed, etc. will increase it. A judicious admixture, however, of rape-seed and cottonseed oils will not affect the density of the sample, but the presence of any considerable proportion of rape-seed oil will sensibly lower the saponification equivalent of it.

Samples of genuine olive oil show an iodine absorption number ranging from 81 to 85, although California olive oil occasionally gives a somewhat higher number. If the iodine number and saponification equivalent correspond to the mean value given in Table I, the oil, as a rule, may be accepted as pure. Should the saponification value correspond, but the iodine number lie above 85, adulteration with sesame, peanut, or cottonseed oil has been attempted, and should the saponification equivalent be lower than the mean in the table, and the iodine number higher, the adulterant is presumably rape-seed oil.

The elaidin test is also of great value. Pure olive oil yields, in less than 2 hours, at a temperature from 15° to 20°, a semisolid mass that cannot be displaced by shaking the bottle, and, within 24 hours, a solid and sonorous, pale-yellow or nearly white mass is produced.

With adulterated samples, the elaidin obtained is orange or dark red, and liquid or semisolid, or, not infrequently, a liquid layer is formed on the surface of the solid elaidin. The elaidin test is applicable to the detection of sesame, rape-seed, cottonseed, poppy-seed, and linseed oils when in admixture with olive oil.

The admixture of hydrocarbon oils to olive oil destined for lubricating purposes is detected according to previous directions. When used for this purpose, the acid number should be determined, and should not exceed 16.

The rise of temperature on treating a sample of olive oil with sulphuric acid is a valuable indication of its purity. Almost all oils, except lard and tallow oils, and cocoanut olein, produce more heat than olive oil, so that a rise of temperature of more than 44° may be considered as indicating probable adulteration.

RAPE-SEED OIL

39. Rape-seed, or **colza, oil** is obtained from the seeds of several species of *Brassica*, of the order *Cruciferæ*. The seeds are commonly subjected to steam heat before pressure, to coagulate the albuminous matter and facilitate the extraction of the oil.

When freshly expressed, rape oil is a yellowish-brown or brownish-green viscid liquid, of a peculiar odor and pungent taste, owing to the foreign matter present. These impurities separate to some extent by keeping the oil, but are not entirely removed by passive treatment. They lessen the combustibility and cause much smoke during combustion. Brown rape oil or sweet rape oil is the commercial name for the oil expressed from the seeds. It is usually refined by treatment with sulphuric acid, and sometimes supplemented by agitation with alkali, and, of late years, a current of steam has been successfully applied. The refined oil is very light yellow and should be almost odorless. It takes an intermediate position between drying and non-drying oil. It does not thicken readily when heated and exposed to air, and yet gives but an imperfect solid elaidin with nitrous acid. In non-drying character, it is decidedly inferior to olive oil, but superior in odor and appearance to the lower qualities of the latter. Notwithstanding a slight tendency to gum, it is extensively used for engine and machinery lubrication, as well as for lighting purposes.

40. Assay of Commercial Rape Oil.—Rape oil is subject to numerous adulterations, the more important of which can be detected with tolerable certainty. The specific gravity of genuine oil averages .915 at 15.5°, and its specific gravity is a valuable indication of its purity, as all the ordinary adulterants are heavier than the genuine oil, with the exception of mineral oils, which can be readily detected and determined according to previous directions. Foreign seed oils of more of less drying character, as sesame, sunflower, cress-seed, hemp-seed, cottonseed, linseed, and possibly cocoanut olein, all range between .920 and .937 in density.

Hence, if the sample has a specific gravity of .918, it may possibly contain even 50 per cent. of these oils, while the smell and color would be but little affected. Seed and nut oils deteriorate rape oil by increasing its gumming properties, with the exception of arachis oil and cocoanut olein, and the addition of either of these is improbable.

The normal values for the iodine number and saponification equivalent, as a rule, together with the specific gravity, suffice for identification. The increase of temperature on treating genuine rape oil with sulphuric acid averages 59°, the extreme variations being from 55° to 66.7°. Any greater rise than that which corresponds to the rise normally yielded by rape oil under the conditions of the experiment may be due to an admixture of cottonseed, hemp-seed, or linseed oil.

With the elaidin test, rape oil behaves in a peculiar and somewhat characteristic manner. Solidification occurs very slowly; but, after 50 or 60 hours, the oil is frequently converted into a pasty mass, which is sometimes yellow, and, in other cases, orange red or mottled. A separation into a solid and liquid portion frequently occurs. The results are much influenced by the temperature. At 10° many samples become apparently solid, but, on being touched with a glass rod, are seen to be a peculiar mixture of liquid and solid. On immersing the bottle containing the product formed at 10° for a short time in water at 15°, the elaidin forms a thick liquid.

The color test with sulphuric and nitric acids are of value for the detection of certain admixtures, such as linseed and fish oils. Richter states that on shaking 5 cubic centimeters of a sample with 1 cubic centimeter of solution of soda of Sp. Gr. 1.34, pure rape oil forms a dirty milky fluid, hemp oil a brownish-yellow thick soap, and train oil a dark-red solution.

CASTOR OIL

41. Castor oil is expressed from the seeds of *Ricinus communis.* It is a transparent, colorless, or pale greenish-yellow liquid with a faint odor and disagreeable taste. At a

low temperature, it thickens, and, at −18°, it solidifies to a yellow mass. It is distinguished in its physical character from most other oils by its high specific gravity and viscosity, ready solubility in alcohol, and insolubility in petroleum spirit. These characteristics are of value for the assay of commercial samples.

42. The peculiar physical characteristics of pure castor oil distinguish it sharply from most other oils, but it is liable to adulterations, which, when not in excessive proportion, are very difficult to detect. The most probable adulterants are poppy oil, lard oil, cocoanut oil, seal oil, rosin oil, and the oxidized, or "blown," oil now manufactured from rapeseed, linseed, and cottonseed oils.

The specific gravity of pure castor oil ranges from .960 to .964, and any sample showing less than .958 is open to suspicion. The only other commercial fixed oil having as high a specific gravity is "blown" oil. Rosin oil has often as high a specific gravity as .998, but it can be readily detected and determined as has already been described. Iodine number, saponification equivalent, and acetyl number, in connection with the specific gravity, serve to determine its purity. The acetyl number should not exceed 15.2.

It is generally claimed that pure castor oil must completely dissolve in 2 parts by volume of 95-per-cent. alcohol. This description is faulty; at a temperature of 30°, it is strictly correct, provided the volume and strength of alcohol and temperature are strictly adhered to, but the use of a slightly weaker alcohol, the addition of the smallest quantity of water, or a slight reduction of temperature causes the castor oil to be thrown out of solution. It is perhaps preferable to use 4 volumes of alcohol at 15° than half that volume at a higher temperature. If any considerable proportion of adulterant is present, the liquid separates, on standing, into three layers, of which the lowest is usually the adulterant and its volume will afford an approximate indication of the proportion of the admixture.

Castor oil is also readily soluble in glacial acetic acid. It is

easily miscible with an equal measure of that solvent at the ordinary temperature; whereas, most other fixed oils, except croton oil, are only dissolved on heating, and yield solutions that become turbid before they have again cooled to the ordinary temperature.

The behavior of castor oil with petroleum spirit is very characteristic. As far as known, all other fixed oils dissolve with facility in this solvent and appear to be miscible in all proportions therewith and with mineral lubricating oil. Castor oil, however, is not soluble in petroleum spirit, though it is itself capable of dissolving its own volume of that liquid. With the heavier petroleum and shale products, castor oil behaves in a similar manner, at least in a qualitative sense. In making a mixed oil for lubricating purposes, the castor oil must first be dissolved in an equal measure of tallow or lard oil, and the heavy mineral subsequently added. If the proportion of this does not exceed that of the castor oil employed, no separation will occur on standing.

SESAME OIL

43. Sesame oil has a yellow color, is thinner than most oils, nearly odorless, and has a bland and agreeable taste. That expressed from the seeds congeals at about $-5°$, but that extracted by solvents congeals at about $+5°$. Its specific gravity ranges from .921 to .924. It is frequently adulterated with cottonseed oil. Neither the iodine number, saponification equivalent, nor the specific gravity affords sufficient means for identification, but the *Livache test* is particularly suited to this purpose. It depends on the fact that the increase in weight due to absorption of oxygen is perceptibly less in the presence of cottonseed oil than in the genuine article.

44. Livache's Test.—The test of Livache is conducted by precipitating the solution of a lead salt with zinc. The precipitate is quickly washed with water, alcohol, and ether, and dried in a vacuum over sulphuric acid. Two quantities of the lead powder, each 1 gram, are spread out in a thin

layer on two large watch glasses. The weight of the glass and powder of each are taken, and, by means of a finely drawn out pipette, 20 drops of the oil in question are placed on one watch glass in such a manner that the drops do not flow together. On the other glass, a similar quantity of sesame oil, known to be strictly pure, is placed and both are again weighed. They are then allowed to stand at the ordinary temperature, in a place exposed to light but protected from dust, for 7 days. When the time has elapsed, the increase in weight of each is determined and reckoned in percentage of the substance. If the substance under examination was pure, the percentage will be the same as that of the standard, but, in the case of adulteration with cottonseed oil, the percentage will be perceptibly smaller.

45. Detection of Sesame Oil in Other Fatty Substances.—Olive oil and sometimes butter are mixed with the cheaper body, sesame oil. The latter is detected with certainty from the red coloration it gives when mixed with furfurol and hydrochloric acid. Instead of furfurol, some body yielding it when subjected to the action of hydrochloric acid, viz., sugar, may be used. It has been found, however, that an alcoholic solution of 2 grams of furfuraldehyde in 100 cubic centimeters of alcohol is the best reagent; $\frac{1}{10}$ cubic centimeter of this reagent is used for each test.

The test is made as follows: The quantity of the furfuraldehyde solution mentioned above is mixed with 10 cubic centimeters of hydrochloric acid, and there is added, without mixing, an equal volume of the suspected substance. On standing, a red coloration is produced at the zone of separation of the two liquids. If the oil is sesame, the coloration is produced instantly. As little as 1 per cent. of sesame oil in a mixed oil will show the color in 2 minutes.

ARACHIS OIL

46. Arachis, earthnut, or peanut, oil is obtained from the nuts of *Arachis hypogæa*, an herb indigenous to America, but now cultivated in various countries, the oil being chiefly

expressed in France. The seeds contain about 45 per cent. of oil, which in India is known as *katchung oil*, and is largely used there as a substitute for olive oil. Arachis oil is usually pale greenish yellow, and of a peculiar nutty flavor and smell, but may be prepared nearly colorless and almost tasteless. It becomes turbid at about 3° and solidifies at about −5°. Its specific gravity ranges between .916 and .920.

47. Arachis oil is characterized by the iodine number and saponification equivalent given in the tables as well as the rise of temperature, which equals 47° to 67° with Maumené's test. Additions of peanut oil to other oils can be detected according to De Negri and Fabris by the fact that the soap solutions obtained in the determination of the saponification number solidify comparatively easy. An olive oil diluted with 10 per cent. of peanut oil after determination of the saponification number gives a turbid liquid that subsequently deposits a precipitate of the potassium salt of arachic acid.

COTTONSEED OIL

48. Cottonseed oil is now produced in enormous quantities in this country and Europe and is used in large quantities in the manufacture of margarine, as adulterant of olive oil, in ointments, and for culinary purposes.

Crude cottonseed oil has a specific gravity of .916 to .930 and contains in solution a characteristic coloring matter, which gives it the ruby-red color. The crude oil gives a bright-red coloration with sulphuric acid and the soap from it rapidly oxidizes on exposure to air with the production of a fine purple or violet-blue color. This reaction is characteristic. It is this coloring matter that causes the oil to produce stains, and it may be removed by shaking the crude oil, at ordinary temperature, with about 10 per cent. of its volume of a solution of caustic soda of Sp. Gr. 1.06, when the alkali combines with the coloring matter and saponifies a portion of the oil. The mixture becomes filled with black flocks, which settle on standing and leave the oil but slightly

colored. The loss from refining is usually from 4 to 7 per cent., although, occasionally, losses of 12 to 15 per cent. occur. It is, therefore, desirable, before purchasing crude cottonseed oil for refining, to make a laboratory test in order to establish approximately the loss that will occur with that particular lot of oil.

Refined cottonseed oil has a specific gravity ranging from .922 to .926, and it solidifies at from 1° to 10°. Its color varies from very pale yellow to golden yellow. By subjecting the oil to cold and pressure, a certain proportion of stearin is separated, and the melting point of the residual oil consequently lowered. This refined oil is usually free from acid, and, when properly prepared, of pleasant taste and well adapted for culinary purposes.

Cottonseed oil is not in itself very liable to adulteration, but is very frequently employed to adulterate other higher priced oils. It may be detected by the specific gravity together with color tests given below and those under Color Reactions of Oils, and in the tables in connection with these articles.

49. Bechi's Test for Detection of Cottonseed Oil. Crude, fresh cottonseed oil, when not too highly colored, as well as the refined oil, may be distinguished from other oils by the peculiar property of reducing silver salts in certain conditions. The test is conducted as follows: Silver nitrate to the amount of 1 gram is dissolved in 200 cubic centimeters of 98-per-cent. alcohol and 40 cubic centimeters of ether, and 1 drop of nitric acid is added to the mixture; 10 cubic centimeters of the oil under examination are shaken in a test tube with 1 cubic centimeter of this reagent, and then with 10 cubic centimeters of a mixture containing 100 cubic centimeters of amyl alcohol and 10 cubic centimeters of rape-seed oil. The mixture is divided into two portions, one of which is put aside for future comparison and the other plunged into boiling water for 15 minutes. A deep brown or black color, due to the reduction of silver, reveals the presence of cottonseed oil. Unless cottonseed oil has

been boiled or refined in some unusual way, the test, as applied above, is rarely negative.

50. Nitric-Acid Test.—On shaking cottonseed oil with nitric acid of Sp. Gr. 1.37 to 1.38, a rich brown coloration is produced. The coloration is equally distinct in the case of oils that have been boiled, and, in this respect, the test is superior to Bechi's. Occasionally, however, samples of American cottonseed oil are found that react so faintly with nitric acid as to make it impossible to detect adulteration by them to the extent of 10 per cent. In doubtful cases, both tests should be applied, and if uncertain results are obtained, Halphen's test, given in Art. **51**, should be used.

51. Halphen's Test.—Carbon disulphide, containing about 1 per cent. of sulphur in solution, is mixed with an equal volume of amyl alcohol. Equal volumes of this reagent and the oil under examination, say 3 cubic centimeters of each, are mixed and heated in a bath of boiling brine for 15 minutes. If no red or orange tint is produced, 1 cubic centimeter of the reagent is added, and, if after 5 to 10 minutes more heating no coloration is produced, another 1 cubic centimeter of the reagent is added, and the boiling continued for 10 minutes. It is possible to detect very small quantities of cottonseed oil by this test.

TALLOW

52. Tallow is commercially classed as *beef* and *mutton* tallow, but each of these comprises the fat of other animals besides the ox and the sheep. Pure tallow is white and almost tasteless, but much of that in commerce has a more or less yellow color and disagreeable rancid flavor. In chemical composition, tallow is very similar to lard, consisting essentially of a mixture of palmitin, stearin, and olein.

53. In addition to the constants, viz., specific gravity, iodine number, and saponification equivalent, the determina-

tion of the freezing point of the fatty acids, the so called *titer test*, is of especial importance. In order to obtain concordant results, the following method was proposed by Wolfbauer: 25 cubic centimeters of potassium-hydrate solution, Sp. Gr. 1.509 (125 grams of potassium hydrate in sticks in 100 cubic centimeters of water), are stirred with 120 grams molten sample in a beaker. The temperature should only vary slightly above the melting point of the tallow. It is placed in an oven at 100°, after being agitated, mixed, and covered with a watch glass where it is permitted to remain, with occasional stirring, until saponification is complete, and a drop warmed with 50-per-cent. alcohol completely dissolves, which is the case after about two hours. 150 cubic centimeters of boiling water are stirred into the soap, which is then poured into a dish, treated with 165 cubic centimeters of sulphuric acid, Sp. Gr. 1.143 (22 cubic centimeters of concentrate sulphuric acid and 150 cubic centimeters of water), and boiled until the fatty acids form a perfectly clear layer.

The acid liquor is withdrawn entirely with a siphon and the fatty acids are boiled with weak sulphuric acid (5 cubic centimeters of concentrate sulphuric acid in 100 cubic centimeters of water), which is again withdrawn, after which they are twice boiled out with 100 cubic centimeters of water. The fatty acids are eventually dried for 2 hours at 100°. The solidified acids are melted in a water bath and filled to within $1\frac{1}{2}$ centimeters into a thin-walled test tube 15 centimeters in length and 3.5 centimeters in diameter. The test tube is then suspended in a specimen bottle by means of a cork. Thereupon a thermometer, graduated to one-fifth degrees as far as 60°, is inserted through the cork into the fatty acids in such manner that, while $\frac{4}{5}$ centimeter distant from the bottom, it is submerged to the 35th division.

The clear mass is stirred with the thermometer until no longer transparent, and until the thermometer reading on repeated stirring no longer changes. The thermometer is then fastened. The mercury begins to rise, due to liberation

of latent heat of fusion. The highest mark that it touches, and at which it becomes stationary, is read off and taken as the "freezing point." The difference between two determinations should not exceed .1°.

The manipulation requires considerable skill and practice. Frequently, the iodine number of the fatty acids of tallow is taken. The number obtained multiplied by 1.1102 gives the oleic acid in the fatty acids. When used for lubricating purposes, tallow should not contain more than .5 per cent. of matter insoluble in chloroform.

WAXES

54. As has been previously mentioned, **waxes** are of animal and vegetable origin. They are partly saponifiable and separate insoluble higher fatty alcohols. Mineral waxes are unsaponifiable. The saponification number affords a sure basis of distinction.

VEGETABLE AND ANIMAL WAXES

55. The following determinations are usually made in the examination of vegetable and animal waxes:

1. Acid number.
2. Saponification number.
3. Ester number, which is the difference between the acid and saponification numbers.
4. Specific gravity.
5. Melting and freezing points.

The determinations are generally conducted according to the methods previously described.

56. Specific Gravity.—The specific gravity of waxes is most conveniently determined by means of a Sprengel tube, which has been explained in *Physics*. A somewhat modified form is shown in Fig. 3, and consists of a **U** tube of about 18 cubic centimeters capacity and 11 millimeters external diameter, which tapers at both ends to

narrow bent tubes *a* and *b*, of which one is longer and is provided with a mark *m*. The molten fat or wax is brought into the tube by suction, as explained in *Physics*. It is then brought into a water bath of constant temperature, until the wax ceases to expand, and the excess in the shorter arm is removed with filter paper, until the longer arm is just filled to the mark. It is allowed to cool, the tube is carefully wiped clean, and weighed. The experiment is repeated with water. The specific gravity from these data is obtained in the usual manner.

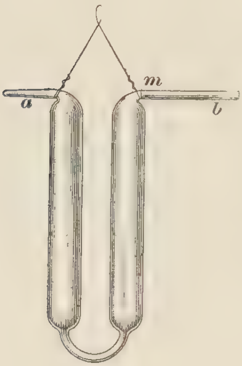

FIG. 3

57. Melting Point.—Many methods have been devised for determining the melting point of fats, but none has been found that really is satisfactory in every respect. The following methods may be recommended for waxes:

The wax is carefully melted in a beaker, and a capillary tube is dipped into the liquid fat, and when filled, one end of the tube is sealed in the lamp and it is then put aside in a cool place for 24 hours. At the end of this time, the tube is tied to the bulb of a delicate thermometer, the length used or filled with fat being the same length as the thermometer bulb. The thermometer and attached fat are placed in water or other transparent media, and gently warmed until the capillary column of fat becomes transparent. At this moment, the thermometric reading is made, and entered as the melting point of the fat.

Another method consists in dipping a thermometer in the molten fat for a moment and thus obtaining the bulb covered with a thin film of the fat. The thermometer is then fixed in a test tube in such a way as not to touch the bottom, and the film of fat warmed by the air bath until it fuses and collects in a little drop at the end of the thermometer bulb, when the temperature is taken.

EXAMINATION OF BEESWAX FOR ADULTERANTS

58. Total Acid Number.—In consequence of the difficulty experienced in the saponification of many waxes with alcoholic potash, especially when they contain paraffin and ceresin, too low results are frequently obtained. Benedict and Mangold therefore determine the "total acid number" instead of the "saponification number," that is, the number of milligrams of caustic potash required to neutralize 1 gram of the mixture of fatty acids and alcohol that is set free from the wax by saponification of the wax and subsequent decomposition of the soap obtained by boiling with dilute hydrochloric acid. The mixture is termed **decomposed wax.**

In order to prepare the latter, 20 grams of potassium hydrate are dissolved in 15 cubic centimeters of water in a hemispherical dish of 350 to 500 cubic centimeters capacity. The solution is heated to boiling, when about 20 grams of the previously melted wax are stirred in. The solution is heated 10 minutes, with constant, brisk stirring, over a small flame; 200 cubic centimeters of water are added, the mass is heated and acidified with 40 cubic centimeters of hydrochloric acid, previously diluted with a little water. Thereupon it is boiled until the upper layer becomes perfectly clear. It is allowed to cool, and is boiled out 3 times with portions of water, to the first of which hydrochloric acid has been added. The cake is finally removed, wiped off with filter paper, is melted in a drying oven, and filtered. The filtered fat is poured, still liquid, on a watch glass, and is broken up after cooling. For the estimation of the total acid number, 6 to 8 grams of the decomposed wax so obtained are covered with alcohol, heated on a water bath, and titrated after addition of phenol phthalein. Even when a large amount of ceresin is present, the saponification is usually complete. The total acid number lies somewhat lower than the saponification number, on an average being about 92.8.

59. Ceresin and Paraffin.—The amonnt of paraffin or ceresin present may approximately be ascertained on the

basis of the total acid number S, by means of the following formula:

$$P = 100 - \frac{100\,S}{92.8}, \qquad (1)$$

where P = paraffin or ceresin, and 92.8 = average total acid number of pure beeswax.

The test of Messrs. Buisine is useful in the exact determination of the paraffin or ceresin. This depends on the fact that the fatty alcohols, on heating with soda lime, disengage hydrogen with the formation of the sodium salts of corresponding fatty acids according to the equation:

$$\underset{\text{cetyl alcohol}}{C_{15}H_{31}CH_2OH} + NaOH = \underset{\text{sodium palmitate}}{C_{15}H_{31}COONa} + 2H_2$$

A subsequent extraction with ether or petroleum spirit removes, besides paraffin and ceresin, only the hydrocarbons of the beeswax, which latter vary from 12 to 14.5 per cent.

To accomplish this, 2 to 10 grams of sample are melted in a small porcelain crucible, and to it is added an equal volume of powdered caustic potash. It is stirred, and on cooling a hard mass is obtained, which is pulverized and uniformly mixed with 3 parts soda lime (for 1 part of wax).

The mixture is then heated in a small flask at 250° for 2 hours. The residue, if necessary, together with the adhering broken glass of the flask, is powdered and extracted in a flask or extractor with ether or petroleum ether. The liquid is filtered, if necessary, the solvent is distilled off, and the last adhering traces of it are vaporized. The residue is then weighed. If p = percentage of hydrocarbons found, and C = ceresin or paraffin, then, if the hydrocarbons in genuine beeswax are taken as 13.5 per cent.,

$$C = \frac{100p - 1{,}350}{86.5} \qquad (2)$$

60. Stearic Acid.—Stearic acid heated with alcohol dissolves, together with ceresin, but, unlike the latter, it does not separate so readily on cooling.

Therefore, if 1 gram of wax be boiled for several minutes with 10 cubic centimeters of 80-per-cent. alcohol in a test

tube 18 to 20 millimeters wide, and allowed to cool to 18° to 20°, then upon adding water to the solution, filtered into a similar test tube, the liquid becomes slightly turbid if it contains pure wax, whereas, when stearic acid is present, a flocculent precipitate is formed. On the strength of the acid number, the stearic acid may be approximately determined by calculation. The acid numbers of pure beeswax and stearic acid are respectively 20 and 195.

If that of the sample = S, then the stearic acid equals

$$K = \frac{100(S-20)}{175} \qquad (3)$$

The absence of other acids is, of course, taken for granted.

MINERAL OILS

61. Mineral oils are either distillation products of bituminous coal or bituminous shales, etc., or else their origin is crude petroleum, from which they are likewise obtained by distillation. Their use is mainly for lubricating and illuminating purposes. The higher distillation products of petroleum or shale, termed **heavy oils**, are used as lubricants, while the lower boiling fractions of shale oil are used for illuminating purposes, under the names of **solar oil, illuminating oil**, and those from crude petroleum, as **petroleum.**

The gas oils, likewise from shale oil, are used mainly in oil-gas factories, while the lowest distillation products (light shale oil, photogen on the one hand, gasolene, naphtha, benzine on the other) are used as solvents for fats, etc.

MINERAL LUBRICANTS

62. The generally accepted conditions of a good lubricant are as follows:

1. Body enough to prevent the surfaces, to which it is applied, from coming into contact with each other.

2. Freedom from corrosive acids, either mineral, animal, or vegetable origin.

3. As fluid as possible consistent with "body."
4. A minimum coefficient of friction.
5. High "flash" and "burning" points.
6. Freedom from all materials liable to produce oxidation or gumming.

In order to identify the oil, whether a simple mineral, animal, or vegetable oil, or a mixture, the viscosity, specific gravity, flash point, burning point, acidity, rosin oils, coal-tar oils, are the tests usually undertaken.

63. Identification of Oil.—Of the oil, 10 grams are weighed out into a dry, weighed beaker of 250 cubic centimeters capacity, and to it are added 75 cubic centimeters of an alcoholic solution of potash (60 grams KOH to 1,000 cubic centimeters of 95-per-cent. alcohol), and the contents evaporated until all the alcohol is driven off. In this process, if any animal or vegetable oil is present, it is formed into a soap by the potash, while the mineral oil is unacted upon. Water, to the amount of 75 cubic centimeters, is then added, and the whole thoroughly stirred to insure complete solution of the soap, and it is then transferred to a separatory funnel, shown in Fig. 4, 75 cubic centimeters of sulphuric ether added, corked, the liquid violently agitated and allowed to stand for 12 hours. Two distinct liquids are now seen, the lower, the solution of the soap, the upper, the ether solution (colored, if mineral oil is present, colorless if not). The aqueous solution is drawn off in a beaker, the ethereal solution remaining in the separatory funnel. The former is placed on a water bath, heated

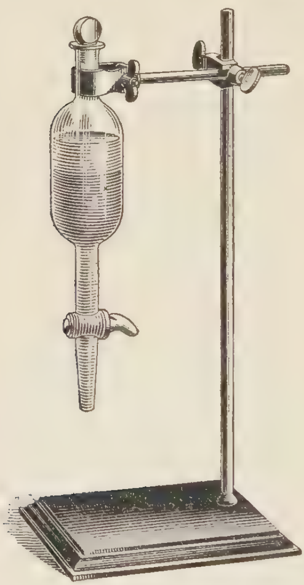

FIG. 4

for half an hour or until all traces of ether are gone. The solution is allowed to cool, diluted somewhat with water, and made acid with dilute sulphuric acid. Any animal or vegetable oil present will be indicated by a rise of the fatty acids to the surface of the liquid.

If it is desired to weigh the fatty acids, proceed as follows: Weigh carefully about 5 grams of pure, white beeswax, place it in the beaker upon the surface of the oil and water, and bring the contents nearly to boiling; the melted wax and fatty acids unite; allow to cool, remove the wax, wash with water, dry between folds of filter paper, and weigh. The increase in weight of the wax over its original weight gives the weight of the fatty acids of the animal or vegetable oil in the lubricating oil. The weight obtained must be multiplied by .97, since the fatty acids exist in the oil as anhydrides and not as hydrates, the latter being the form in which they are weighed.

64. Instead of weighing the animal or vegetable oil, some chemists prefer to make use of the ether solution, determining the hydrocarbon oil directly, in which case the mode of procedure is as follows: After drawing off the soap solution from the separatory funnel, the ether solution is run into a weighed flask of about 250 cubic centimeters capacity, and the ether distilled off. The residue in the flask now consists of the mineral oil and some water.

It is quite difficult to get rid of all this water. Direct heating is inadmissible, since the water spurts up, throwing the oil out of the flask, causing the oil to be lost. To overcome this place a glass tube through the stopper, in the shape of the letter **S**. Any oil ejected against the tube or cork cannot escape, but returns to base of flask, while the heat is gradually increased in the flask and the water vaporized and passed out through the tube; three to four weighings are generally required before a constant weight is obtained. The former process is preferable, since it is performed much more rapidly than the latter, and the animal and vegetable oils are positively shown and can generally be identified.

Many lubricating oils contain as high as 20 per cent. of hydrocarbon oil, volatile at or below 100°. It is, of course, in the ether solution, and when the water is expelled from the oil, after the ether has been driven off, that a large proportion of the volatile hydrocarbon is vaporized. If, now, the animal or vegetable oil is not also determined, a serious mistake would be made, viz., reporting 20 per cent. of animal oil when it is volatile mineral oil.

65. Viscosity.—A useful physical test for oils is based on their relative **body**, or **viscosity**, a property that may be regarded as the converse of fluidity.

The first instrument for the determination of the viscosity of oils was probably that of Schubler. It consisted of a glass cylinder, open at the top, and drawn to a $\frac{1}{32}$-inch tube at the bottom. Having filled the cylinder with the oil to be tested, the time required for 100 cubic centimeters of the oil to flow out through the aperture was noted, and this figure was compared with that obtained from water under similar conditions, the latter being taken as 1.

The Pennsylvania Railroad Company's viscosity tests are made as follows: A 100-cubic-centimeter pipette is graduated to hold just 100 cubic centimeters to the bottom of the bulb. The size of the aperture at the bottom is then made such that 100 cubic centimeters of water at 37.5° will run out of the pipette down to the bottom of the bulb in 34 seconds. The pipette being obtained, the oil sample is heated to the required temperature, care being taken to have it heated uniformly, when it is drawn up into the pipette to the proper mark. The time occupied by the oil in running out, down to the bottom of the bulb, gives the test figure. A stop watch is convenient, but not essential, in making the test.

These pipettes, known as **Dr. Dudley's viscosity pipettes,** are used in many railroad laboratories in this country, but they are rather difficult to clean, and are not as convenient as the **Engler viscosimeter,** which is shown in Fig. 5. The vessel containing the oil under examination consists of a smooth box A of brass, provided with a lid A'.

Connected with the bottom is a 20-millimeter tube *a*, which is almost exactly 3 millimeters in width. It is usually made of brass, and is open at the top. It may be opened and closed by the plug *b*. Filled to the mark, the apparatus should hold 240 cubic centimeters. The box *A* is surrounded

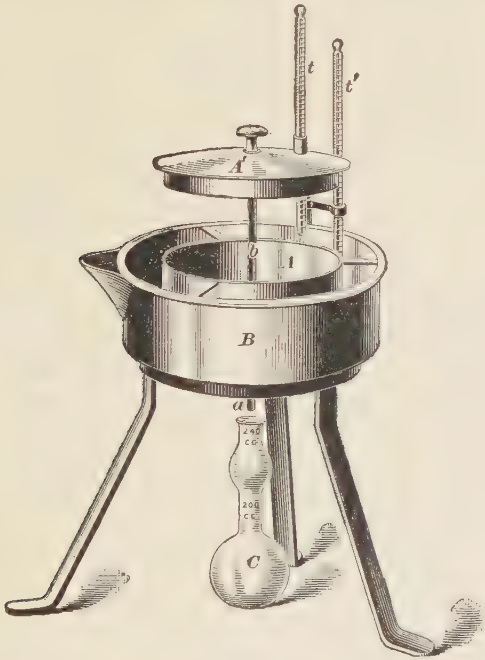

FIG. 5

by a jacket *B* made of brass, and is open at the top. This serves to hold suitable fluid, by which the contents of *A* can be brought to the desired temperature. The thermometers *t* and *t'* record the temperature of the oil to be tested and the liquid in the jacket. The apparatus rests on a tripod. The measuring flask *C*, under the exit tube, is provided in its neck with the marks 200 and 240.

Regulation of the Apparatus.—Water, to the amount of 240 cubic centimeters, is placed in the box, which has previously been cleaned with ether, alcohol, and water, and

plugged. The temperature is brought to 20°. To do this, the water contained in the jacket *B* is maintained at this temperature until the inner thermometer registers 20°. In the meanwhile, the flask is allowed to drain. It is then placed under the vent and the plug is withdrawn. The time that elapses while the flask is being filled to the 200-cubic-centimeter mark is recorded in seconds. The time required to issue should be between 50 and 55 seconds, when the apparatus is properly constructed. The mean is taken of three determinations, which should not differ more than 15 seconds. This time is taken as 1.

Oil Test.—In the next operation, all moisture is removed from the box by drying and rinsing with alcohol, and then with ether. The apparatus is filled to the mark with the oil in question. It is then brought to the desired temperature by heating the jacket *B*, which may contain either water or oil. The temperature of the oil under examination must remain constant for at least 3 minutes before the operation is begun. Determination of the time of issue is then conducted as before.

The lowest grade of an oil that is to be used as a lubricant has, according to Engler, a degree of viscosity of 2.6 at 20°, when water = 1. With viscosity determination of lubricants, the rule holds good that the temperature used should lie near that which the oil will assume while in use (machine oil 50°, cylinder oil 150°, etc.).

Fatty oils, as well as lubricants, are subjected to viscosimetric tests. In many cases, such as rape-seed oil, for instance, the viscosity is so large and so constant that it may serve as a test for purity.

66. Specific Gravity.—The specific gravity of lubricants may vary within wide limits. As a rule, the greater the specific gravity of an oil, the higher will be its flash point and viscosity; but there are many exceptions. Lubricating oils from Russian petroleum have a higher viscosity than the products of similar density from American petroleum and shale oil. In the case of oils completely fluid at

ordinary temperature, the specific gravity may be determined by any of the usual methods. The density of the thicker and semi solid oils is best ascertained by filling a specific-gravity bottle to the brim with the warm oil. When it has cooled to a temperature of 15.5°, the stopper is inserted, and worked to and fro until it is forced home, the excess of oil gradually escaping through the perforation in the stopper, when the bottle may be wiped clean and weighed.

67. Flash and Burning Points.—The flash point is the degree of temperature at which ignitible volatile vapors are given off by an oil, producing a flash when brought into contact with a small flame. The fire test or determination of burning point is simply a continuation of the flash test until the oil permanently ignites. The mode of procedure is as follows: A porcelain crucible, 6 centimeters upper diameter and 6 centimeters high, is filled with the oil within 1 centimeter of the rim. The mercury bulb of a thermometer is then immersed, with the end 1 centimeter above the bottom, which is best accomplished by first resting the thermometer on the bottom of the crucible and subsequently raising it 1 centimeter. The crucible is warmed in a sand bath, and when the temperature has overstepped 120°, a small flame is passed over the surface of the oil at the same height as the crucible rim at every increase of 5°. As soon as the first faint explosion of oil-vapor-saturated air ensues, the flash point has been reached. The flame is enlarged, and when the temperature has increased 10° to 15°, it is passed over the surface at every 2° increase, until quiet ignition takes place. The burning point is so obtained. Drafts are prevented by screens of pasteboard.

The Standard Oil Company and the New York Produce Exchange use Saybolt's oil tester, which is furnished with an electric battery, where the oil is ignited by electric sparks passing over the oil.

The burning point of spindle oils should not lie under 150°, and that of machine oils not below 170°.

68. Acidity.—Mineral oils should be entirely free from acids. The acid remaining after the refining process is detected by shaking about 100 cubic centimeters of oil with an approximately equal volume of tepid water to which several drops of methyl orange have been added. The aqueous layer, after settling, will appear red.

69. Resins.—Incompletely refined oils resinify readily. A test for resinous matter can be conducted by placing 20 cubic centimeters of the oil, together with 10 cubic centimeters of sulphuric acid and 20 cubic centimeters of petroleum benzine, in a cylinder divided into 50 cubic centimeters, agitating, and allowing to settle. The increase in volume of the sulphuric acid is read off. With good oils, the increase usually amounts to 1.2 to 2.4 cubic centimeters; that is, 6 to 12 per cent. of the oil volume. Under no condition must it exceed 2.4 cubic centimeters, or 12 per cent.

The freezing point of an oil, which in use is subjected to winter temperature, is usually ascertained. Furthermore, the lubricating value is frequently determined by means of special complicated physical apparatus.

PETROLEUM (ILLUMINATING OIL)

70. Kerosene is the refined product from petroleum that distils over (in the refining process) after the lighter oils, naphtha, etc., have been separated, and is the principal oil in use for illumination. In color, it varies from standard white to water-white (colorless), and its commercial value is dependent upon its flash and burning point. In the oil trade, the burning or fire tests are classified as 110° F., 120° F., 150° F., and 300° F. The 150° F. is known as **headlight oil,** and the 300° F., as **mineral sperm** and **mineral colza.**

The requirements for mineral oils to be used in railroad illumination are as follows:

150° F. Fire-Test Oil

The oil must conform to the following requirements:

1. It must have a flash test above 125° F.
2. It must have a fire test not below 150° F.
3. It must have a cloud test not above 0° F.
4. It must be water-white in color.
5. Its gravity must be between 44° and 48° Baumé at 60° F.

300° F. Fire-Test Oil

The oil must conform to the following requirements:

1. It must have a flash test above 250° F.
2. It must have a fire test not below 300° F.
3. It must have a cloud test not above 32° F.
4. It must be standard white in color.
5. Its gravity must be between 38° and 42° Baumé at 60° F.

71. Cloud Test.—The cloud test is made as follows: Of the oil, 2 ounces are placed in a 4-ounce sample bottle, with a thermometer suspended in the oil. The bottle is exposed to a freezing mixture of ice and salt, and the oil stirred with the thermometer while cooling. The temperature at which the cloud forms is taken as the cloud test.

72. The requirements for the flash and fire tests for illuminating oil used for domestic purposes are not so rigid as for railroad practice. In fact, large quantities of oil, flashing below 110° F. are used, the cheaper price being an incentive. So dangerous are these oils with low flash points, that many states have passed stringent laws against their use. An oil with a fire test of 110° F. very often has a flash test of 90° F., and many oils with a fire test of 120° F. flash at or below 100° F. It is the flash point of an oil that makes it dangerous, and while the refiners of oils mark their product by the fire test, the law passed by many states specify the flash test as the requisite.

There is no absolute ratio between the flash and fire test of an oil, since while many illuminating oils have a high fire

and flash test, others may have a high fire and a low flash test.

73. Wisconsin Oil Tester.—The instrument that gives the best satisfaction in testing illuminating oils for the flash and fire tests is called the **Wisconsin oil tester,** and is shown in Fig. 6. It is officially described as follows: On the left side of the figure is shown the instrument entire. It consists of a sheet-copper stand $8\frac{1}{2}$ inches high, exclusive of the base, and $4\frac{1}{2}$ inches in diameter. On one side is an aperture $3\frac{1}{2}$ inches high, for introducing a small spirit lamp *A* or, better, a small Bunsen burner. The water bath *D* is also of copper, $4\frac{1}{8}$ inches high and 4 inches inside diameter. The opening in the top is $2\frac{7}{8}$ inches in diameter. It is also provided with a flange $\frac{1}{4}$ inch wide, which supports the bath in the cylindrical stand. The capacity of the bath is about 20 fluid ounces, this quantity being indicated by a mark on the inside. *C* represents the copper oil boiler. The lower section is $3\frac{3}{8}$ inches high and $2\frac{3}{4}$ inches inside diameter. The upper part is 1 inch high and $3\frac{3}{4}$ inches in diameter, and serves as a vapor chamber. The upper rim is provided with a small flange, which serves to hold the glass cover in its place. The oil holder contains about 10 fluid ounces, when filled to within $\frac{1}{8}$ inch of the flange which joins the oil cup and the vapor chamber. In order to avoid

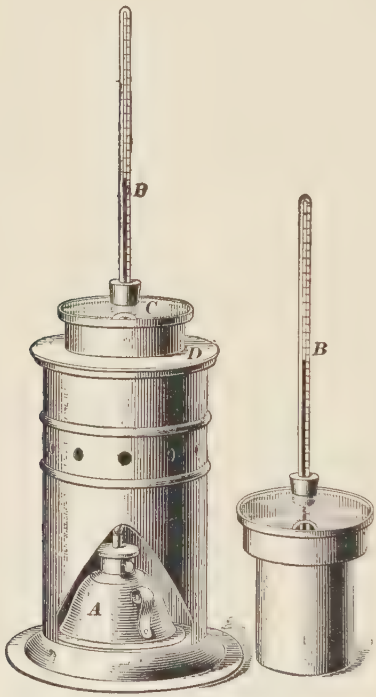

FIG. 6

reflection from the otherwise bright surface, the oil cup is blackened on the inside.

The cover *C* is of glass, and is $3\frac{5}{8}$ inches in diameter; on one side is a circular opening closed by a cork, through which the thermometer *B* passes. In front of this is a second opening $\frac{3}{4}$ inch deep, and $\frac{3}{4}$ inch in width on the rim, through which the flashing jet is passed in testing. A small jet, $\frac{1}{4}$ inch in length, furnishes the best means for igniting the vapor. Where gas cannot be had, the flame from a small waxed twine answers well.

74. The test should be applied according to the following directions: Remove the oil cup and fill the water bath with cold water up to the mark on the inside. Replace the oil cup and pour enough oil to fill it within $\frac{1}{8}$ inch of the flange joining the cup and the vapor chamber above. Care must be taken that the oil does not flow over the flange. Remove all air bubbles with a piece of dry paper. Place the glass cover on the oil cup, and so adjust the thermometer that its bulb shall be just covered by the oil.

If an alcohol lamp is employed for heating the water bath, the wick should be carefully trimmed and adjusted to a small flame. The rate of heating should be about 2° per minute, and in no case should it exceed 3°.

As a flash torch, a small gas jet, $\frac{1}{4}$ inch in length, should be employed. When gas is not at hand, employ a piece of waxed linen twine. The flame in this case, however, should be small. When the temperature of the oil has reached 85° F., the testings should commence. To this end, insert the torch into the opening of the cover, passing it in at such an angle as to well clear the cover, and to a distance about half way between the oil and the cover. The motion should be steady and uniform, rapid, and without pause. This should be repeated at every 2° rise of the thermometer, until the temperature has reached 95°, when the lamp should be removed and the testings should be made for each degree of temperature until 100° F. is reached. After this, the lamp may be replaced, if necessary, and the testings continued for each 2°.

The appearance of a slight bluish flame shows that the flashing point has been reached.

In every case, note the temperature of the oil before introducing the torch. The flame of the torch must not come in contact with the oil. The water bath should be filled with fresh, cold water for each separate test, and the oil from a previous test carefully wiped from the oil cup.

75. The test for ascertaining the igniting point should be conducted as follows: Fill the cup with the oil to be tested to within $\frac{3}{8}$ inch of the flange joining the cup and the vapor chamber above. Care must be taken that the oil does not flow over the flange. Place the cup into the cylinder, and adjust the thermometer so that its bulb shall be just covered by the oil. Place the lamp or gas burner under the oil cup. The rate of heating should not exceed 10° a minute below 250° F., nor exceed 5° a minute above this point. The testing flame described in the direction of ascertaining the flashing point should be used. It should be applied to the surface of the oil at every 5° rise in the thermometer, until the oil ignites.

76. Viscosity.—According to Engler, the viscosity of illuminating oil bears a direct relation to the speed of absorption in the wick. To conveniently determine this speed in an oil, therefore, the viscosity is taken. The Engler apparatus (shown in Fig. 5), possessing, however, a 1.8-millimeter exit, instead of 3 millimeters, is used.

77. Distillation Test.—The distillation test is conducted in a distilling bulb, shown in Fig. 7, having the following dimensions: Diameter of bulb, 6.5 centimeters; diameter of neck, 1.6 centimeters; length of neck, 15 centimeters. The side tube should be 10 centimeters long, .6 centimeter wide, and attached at an angle of 75°. The distance from the place of attachment to the level of the 100 cubic centimeters of oil, with which the flask is filled, should be 9 centimeters. The side tube is attached to a condenser of 1 centimeter average width, and 45 centimeters in length;

100 cubic centimeters of petroleum are placed in the bulb with a pipette, and are heated to boiling. A wire gauze is set under at first, but is removed when the temperature has risen above 150°. Distillation is conducted so that 2 to $2\frac{1}{2}$ cubic centimeters distil over every minute. The fractions between every 25° or 50° are weighed or measured. As soon as a temperature of 150° is reached, the temperature is allowed to fall at least 20° by removing the lamp. The contents are again brought to boiling, and are distilled until the above temperature is again reached. This is repeated until nothing more distils over at that point. Results agreeing within 1 per cent. are thus obtained. The main fraction, distilling over at from 150° to 300°, is termed *illuminating oil*, which, in especially well refined illuminating oils, can reach 80 and even 90 volume per cent. A good illuminating oil should contain (according to Beilstein) not more than about 5 per cent. fraction under 150°, and not more than about 15 per cent. fraction above 270°.

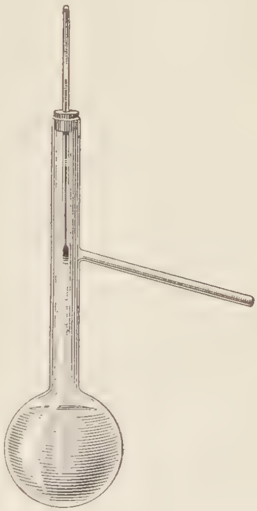
FIG. 7

The test for acids can be conducted according to the method described under lubricating oils. The behavior toward concentrate sulphuric acid is at times used as a test for purity of petroleum. On mixing with an equal volume of concentrate sulphuric acid, and allowing to separate, the petroleum layer should be rather lighter, and the sulphuric acid at the most only yellow, but never brown. The rise of temperature on mixing should not exceed 5°. A rise of temperature of 20° to 50° ensues when distillates of bituminous shales, rosin, etc. are present.

ANALYSIS OF BLEACHING POWDER

78. Bleaching powder, or chloride of lime, is formed by the action of chlorine on calcium hydrate. The relation of its constituents in the freshly prepared substance is represented by the formula $Ca(ClO)_2\ CaCl_2$. When allowed to stand in contact with air and light, chloride of lime suffers decomposition, and, after treatment with water, the calcium chloride is found to have increased in quantity, while the hypochlorite has suffered a corresponding diminution. When exposed to moist air containing carbon dioxide, bleaching powder is decomposed, hypochlorous acid is evolved, and calcium carbonate formed. When, therefore, chloride of lime is used as a disinfectant, the active agent in ordinary circumstances is hypochlorous acid, and not free chlorine. At a moderate temperature (50°), dry chloride of lime is converted into calcium chlorate, and the mass becomes pasty from the absorption of water:

$$3Ca(ClO)_2 = 2CaCl_2 + Ca(ClO_3)_2$$

Since the value of commercial bleaching powder depends entirely on the amount of hypochlorous acid that it can produce, and since the circumstances of heat, moisture, and exposure to air and light exercise such an important influence upon the proper production and stability of the bleaching powder, it is evident that, as manufactured and stored, it must vary very considerable in quality. The most concentrated preparation that can be obtained by saturating calcium hydrate with chlorine contains 38.5 per cent. of available chlorine, but the great bulk of the substances found in commerce rarely contain more than from 32 to 37 per cent., of which 1 or 2 per cent. is without bleaching power, being present in the form of calcium chlorate. In badly made bleaching powder, the amount of chlorate present is

occasionally as low as 8 to 10 per cent. of available chlorine —nearly one-fourth the amount that ought to be present in the product. Many methods have been proposed to estimate the available chlorine present in bleaching powder, the majority being based on the oxidizing effect of the hypochlorites, but a great number are inaccurate, as they do not take cognizance of the presence of this admixed chlorate, which, under the circumstances of the valuation processes, reacts like chlorine, although it has no bleaching effect.

DETERMINATION OF AVAILABLE CHLORINE

79. Penot's Method.—This process is based on the conversion of an alkaline arsenite, by the chloride-of-lime solution, into an arseniate:

$$As_2O_3 + Ca(ClO)_2 \cdot CaCl_2 = As_2O_5 + 2CaCl_2$$

The final point of the reaction is determined by means of potassium iodide and starch; so long as any hypochlorite remains undecomposed, a drop of the solution brought into contact with potassium iodide and starch renders that mixture blue.

80. Preparation of Test Paper.—Three grams of potato or wheat starch are rubbed into a thin cream with 50 or 60 cubic centimeters of warm water. This mixture is poured into 200 cubic centimeters of water, and the liquid heated, under constant stirring, until it boils; 1 gram of potassium iodide and 1 gram of pure carbonate of soda, dissolved in a little water, are added, and the mixture diluted to 500 cubic centimeters. A number of strips of Swedish filter paper are moistened with this solution, and, when dry, are ready for use.

81. Preparation of Standard Arsenious Acid.—To prepare the arsenious-acid solution, powder a quantity of pure, white arsenic As_2O_3, and weigh off exactly 4.95 grams into a liter flask; to this, add from 25 to 30 grams of pure, crystallized, sodium carbonate and 200 cubic centimeters of

water. Boil the solution gently, and shake continually until all is dissolved; cool and dilute up to the liter mark; 1 cubic centimeter of this solution corresponds to .00355 gram of available chlorine, as may be seen from the following:

$$As_2O_3 + Ca(ClO)_2 \cdot CaCl_2 = As_2O_5 + 2CaCl_2$$

1 molecule of As_2O_3 can take up 2 atoms of oxygen to form As_2O_5, which are equivalent to 4 atoms of chlorine.

$$\text{Molecular weight of } As_2O_3 = 198$$
$$\text{Molecular weight of } Cl_4 = 142$$

Since 1 cubic centimeter of the arsenious solution contains

$$.00495 \text{ gram } As_2O_3 = \frac{4.950 \text{ grams taken}}{1{,}000 \text{ c. c. in 1 liter}};$$

then, $$198 : 142 = .00495 : .00355$$

Since it is difficult to weigh out exactly the required quantity of white arsenic, it is preferable to take a round number, about 5 grams, and dilute accordingly. For example, 5.016 grams of white arsenic were weighed out into the liter flask, 30 grams of sodium carbonate and 200 cubic centimeters of water added; after complete solution and cooling, the liquid was diluted to 1 liter and 13.33 cubic centimeters of water were added by means of a burette, since,

$$4.95 : 1{,}000 = 5.016 : 1{,}013.33$$

The solution in the flask is well shaken, and decanted off into a number of small, well stoppered bottles; this precaution diminishes the liability of the solution to change on exposure to the air.

82. Analysis.—Weigh out 10 grams of the bleaching powder, transfer to a mortar, add 50 or 60 cubic centimeters of water, and rub to a thin cream. Allow the heavier particles to settle, decant the turbid supernatant liquid, add more water, rub up again, and continue thus until all the powder has been transferred to a liter flask. Fill the flask up to the mark and shake well. Transfer 50 cubic centimeters of this solution, by means of a pipette, to a beaker, and add the arsenious solution, from a burette, with constant stirring. The end of the reaction is determined by means

of starch and potassium iodide, used as an outside indicator. After each addition of the arsenious solution, the mixture is stirred, and a drop is removed upon a glass rod, and brought into contact with a piece of the filter paper, prepared according to the directions previously given. So long as undecomposed bleaching powder is present, the liquid will cause a blue stain upon the paper. The arsenious solution is cautiously added, until a drop of the liquid brought into contact with the paper gives no blue stain. There is no difficulty in observing the final point; the gradual increasing faintness in the blue color of the drops indicates with great accuracy the progress of the reaction. In making a second reaction, care must be taken to shake the contents of the liter flask, before withdrawing the solution; if this precaution is neglected, the second determination will give a much lower result—a difference of 2 or 3 cubic centimeters being not infrequently obtained in testing the clear and the turbid liquids.

For example, 10.99 grams of bleaching powder were treated as described, and diluted to 1 liter; 50 cubic centimeters of the turbid solution required 48.1 cubic centimeters of the arsenious solution to complete the reaction. Since 1 cubic centimeter of this solution is equivalent to .00355 of chlorine, this would correspond to $48.1 \times .00355 = .1707$ gram in the 50 cubic centimeters of solution. But 50 cubic centimeters contain .5495 gram of the bleaching powder, hence, the substance contains $\frac{.1707 \times 100}{.5495} = 31.06$ per cent. of available chlorine.

83. Iron Method.—Weigh out 10 grams of bleaching powder, place in a mortar, add about 50 cubic centimeters of water, rub to a cream; allow the coarser particles to subside, pour off the turbid, supernatant liquid into a liter flask, add more water, and rub again, and continue until the whole lot of the bleaching powder has been transferred to the flask, fill up to the mark, shake well, and remove 50 cubic centimeters, by means of a pipette, to a beaker for analysis.

Weigh out, in the meantime, .325 gram of piano wire, which will contain .324 gram of Fe, and dissolve it in 2 cubic

centimeters of concentrate sulphuric acid, and diluted with 10 cubic centimeters of water. Cool, fill the flask with cold water, and pour into a large beaker. Now add the 50 cubic centimeters of the turbid bleaching powder solution, pouring it in slowly and stirring constantly. Dilute the whole to about 500 cubic centimeters. Then, by means of a standardized solution of potassium permanganate, prepared as described under the heading Volumetric Determinations, determine the iron still remaining in the ferrous condition.

The reaction is

$$4FeSO_4 + Ca(ClO)_2 \cdot CaCl_2 + 2H_2SO_4$$
$$= 2Fe_2(SO_4)_3 + 2CaCl_2 + 2H_2O$$

from which is seen that 56 parts of Fe are equivalent to 35.5 parts of Cl.

For an example, assume that 1 cubic centimeter of the potassium-permanganate solution was equivalent to .003 gram Fe, and that 23.8 cubic centimeters of that solution were required to oxidize the ferrous iron not acted on by the bleaching powder used, in an amount equivalent to .5 gram; 23.8 cubic centimeters of permanganate correspond to $23.8 \times .003$, or .0714 gram of iron remaining unoxidized. Then, .324 (Fe taken) $-$ .0714 (Fe unoxidized) $=$ .2526 gram Fe oxidized by bleaching powder. Since 56 parts Fe correspond to 35.5 parts Cl, we have the proportion: $56 : 35.5 = .2526 : x$, when $x = .1601$ gram available Cl. .5 gram bleaching powder contains .1601 gram available chlorine, therefore 1 gram contains .3202 gram, or 32.02 per cent. available chlorine.

A SERIES OF QUESTIONS AND EXAMPLES

Relating to the Subjects
Treated of in This Volume

It will be noticed that the pages of the Examination Questions that follow have been given the same section numbers as the Instruction Papers to which they refer. No attempt should be made to answer any of the questions or to solve any of the examples until the Instruction Paper having the same section number has been carefully studied.

QUANTITATIVE ANALYSIS

(PART 4)

EXAMINATION QUESTIONS

(1) From a sample of mineral weighing .625 gram, a precipitate of ZnO weighing .1505 gram is obtained. What per cent. of zinc does the mineral contain ?

(2) How may the calcium in natrolite be determined ?

(3) Briefly describe the method of determining water in in prehnite.

(4) If 1 gram of a substance yields .225 gram of Fe_2O_3, what percentage of FeO does it contain ?

(5) What weight of lime can be obtained from 2,000 pounds of limestone containing 90 per cent. of calcium carbonate ?

(6) What are the principal constituents of limestone ?

(7) Outline a method for the analysis of limestone, mentioning only the constituents usually determined.

(8) Give the composition of feldspar.

(9) Give a short method for the determination of carbon dioxide in limestone.

(10) How would you separate the iron and alumina in a sample of limestone ?

(11) (*a*) What is zinc blende ? (*b*) What impurities does it frequently contain ?

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(12) Describe the method of determining the alkalies in insoluble silicates, such as feldspar.

(13) (*a*) What are the chief constituents of chalcopyrite? (*b*) What impurities does it frequently contain?

(14) If a sample of limestone contains 40 per cent. of carbon dioxide, how many cubic centimeters of the gas can be obtained from 1 gram of the stone?

(15) Outline a method for the determination of iron, zinc, and manganese in zinc blende.

(16) In the analysis of chalcopyrite, zinc, cobalt, and nickel sometimes have to be separated; how may the zinc be precipitated from a solution containing these three metals, leaving the cobalt and nickel dissolved?

(17) Referring to question 16: (*a*) Why is sodium-acetate solution added during the precipitation of the zinc? (*b*) Why must the amount of sodium acetate added be limited?

(18) Outline a method for the analysis of a pure sample of chalcopyrite?

(19) Give the composition of wolframite?

(20) How would you determine tungsten?

ACTUAL ANALYSIS

(21) Make a complete qualitative and quantitative analysis of the chemical compound contained in bottle labeled "Quantitative Analysis, Part 4, Question 21."

(22) Make a complete analysis of the chemical compound contained in bottle labeled "Quantitative Analysis, Part 4, Question 22."

(23) Make a complete analysis of the chemical compound contained in bottle labeled "Quantitative Analysis, Part 4, Question 23."

(24) Analyze the sample of limestone contained in bottle labeled "Quantitative Analysis, Part 4, Question 24," and give an outline of your method of analysis, together with your results.*

(25) Analyze the sample of zinc blende contained in bottle labeled "Quantitative Analysis, Part 4, Question 25," and send an outline of the method employed, with your results.

(26) Make a complete analysis of the sample of brass contained in bottle labeled "Quantitative Analysis, Part 4, Question 26."

(27) Make a complete analysis of a silver coin, and send a description of the coin used, together with your results.

(28) Make a complete analysis of a nickel coin, and send a description of the coin used, with your results.

NOTE.—A dime and a five-cent nickel piece are recommended for question 27 and 28, respectively, but the student may use any coin he wishes. A description of the coin used must accompany the results, however.

* Only the constituents usually determined are required.

QUANTITATIVE ANALYSIS

(PART 5)

EXAMINATION QUESTIONS

(1) On what does the value of an iron ore depend?

(2) What determinations are usually made in the analysis of pig iron?

(3) What is used to dissolve the sample of steel in determining the total carbon by combustion?

(4) Describe the selection of a sample of pig iron.

(5) (*a*) For what is silver sulphate used in the determination of carbon in steel? (*b*) How is it prepared for this purpose?

(6) Should the same sample of coal be used for the determination of moisture and volatile combustible matter?

(7) Describe the process known as quartering.

(8) (*a*) What is the objection to a cast-iron mortar and pestle for grinding iron ores? (*b*) What would you substitute in place of these?

(9) For what purpose is a starch solution used in the determination of sulphur in iron and steel?

(10) (*a*) What is Eschka mixture? (*b*) For what is it used?

(10) Discuss the significance of chlorine in drinking water.

(11) Discuss the significance of nitrates in potable water.

(12) If called on to examine the water of a town supply, state, fully, how you would collect the sample.

(13) How would you examine a piece of ice to determine its purity?

(14) What determinations are usually made in the analysis of clay?

(15) Describe the determination of free and albuminoid ammonia in water.

(16) What are the principal scale-forming constituents found in water used as a boiler supply?

(17) Of what is clay composed?

(18) (*a*) What do you understand by the term absolute water? (*b*) How is it prepared?

(19) What color is produced when a naphthylamine solution is added to a sample of water that contains nitrites?

(20) Describe a method of determining lead in ores.

QUANTITATIVE ANALYSIS

(PART 7)

EXAMINATION QUESTIONS

(1) A gas occupies at 22° and 771 millimeters pressure 11.2 liters; what is its true volume at normal temperature and pressure?

(2) What reagent is used to absorb oxygen in gas analysis?

(3) How are the chlorides determined in urine?

(4) How is hydrogen determined in gases?

(5) How may gas analyses, in general, be classified?

(6) What reagent is used to absorb carbon monoxide in gas analysis?

(7) How may sulphur dioxide be estimated in furnace gases?

(8) In estimating the amount of urea in a sample of urine with Hüfner's apparatus, 2 cubic centimeters of urine was taken, and 12 cubic centimeters of nitrogen was obtained. The pressure was found to be 767 millimeters, and the temperature 13°. The specific gravity of the sample is 1.021. What is the percentage of urea in the sample?

(9) A gas saturated with moisture when measured at a temperature of 12° and a pressure of 765 millimeters is found to occupy 97 cubic centimeters. What is its true volume?

(10) What are the principal determinations usually made in quantitative urinary analysis?

(11) Explain the use of Lunge's nitrometer.

(12) How would you prepare a standard sodium-thiosulphate solution, 1 cubic centimeter of which is equal to 1 cubic centimeter of SO_2?

(13) How is Fehling's solution made, and to how much sugar is 1 cubic centimeter of this solution equivalent?

(14) How is urea determined in urine?

(15) In determining the CO_2 in gases, making two estimates a day (600 a year), 50 cubic centimeters of gas at normal temperature and pressure is used in each determination. Of this volume, 20 per cent. was found to be CO_2 in the average. How much KOH was used annually?

(16) How is sugar determined in urine?

(17) What determinations are usually made in the analysis of chimney gases?

(18) How is palladiumized asbestos prepared?

QUANTITATIVE ANALYSIS

(PART 8)

EXAMINATION QUESTIONS

(1) What do you understand by potential ammonia in connection with fertilizers?

(2) What reagent is used for the clarification of a sugar solution before it is polarized?

(3) How is the phosphoric acid present in fertilizers classified?

(4) A sample of green syrup, containing invert sugar, is polarized, and shows an angle of polarization of $+86°$ before inversion, and, after being inverted, an angle of $-19°$. The temperature during polarization was $27°$. What percentage of cane sugar is contained in the sample?

(5) What are the chief determinations made in the analysis of milk?

(6) What does the term coefficient of purity, used in the analysis of sugar beets, express?

(7) Describe the determination of iron oxide and alumina in phosphate rock.

(8) What is the average specific gravity of milk?

(9) What is the normal weight of sugar used with most polariscopes?

(10) Describe the determination of nitrogen by Kjeldahl's method.

(11) How may annatto and saffron be detected, when employed in the coloration of butter?

(12) How is sugar extracted from beets for the purpose of analysis?

(13) Outline Babcock's method for the determination of fat in milk.

(14) Describe a simple process that may be successfully used for the detection of butter adulteration.

(15) The specific gravity of a sample of milk is 1.0328, and the percentage of fat was found to be 2.56. What is the percentage of total solids?

(16) How would you determine sulphur in pyrite?

(17) Show, by an equation, how cane sugar is inverted by hydrolysis, and state what the products of this inversion are.

(18) A sample of raw sugar polarizes, before inversion $+69°$, after inversion $-24°$, at a temperature of 22°. For Meissl and Hiller's determination, 3.5 grams of the sample were used, and 315 milligrams of *Cu* were obtained. What is the percentage of cane sugar and invert sugar in this sample?

(19) State how the qualitative test for invert sugar is performed.

(20) Can the specific gravity of milk be considered as an indisputable indicator of the quality of milk?

QUANTITATIVE ANALYSIS

(PART 9)

EXAMINATION QUESTIONS

(1) The percentage of hydrocarbon in a sample of beeswax was found to be 15; what is the percentage of ceresin in the sample?

(2) In an analysis of bleaching powder, to determine its available chlorine, 11.5 grams has been analyzed. For the determination, a standardized solution of arsenious acid was used, 1 cubic centimeter of which is equivalent to .0033 gram of chlorine; 50 cubic centimeters of the bleaching powder in a 1,000-cubic-centimeter solution was titrated, and 47.4 cubic centimeters of the arsenious solution was required. What is the percentage of available chlorine in the sample?

(3) What does the acetyl number represent, and how is it determined?

(4) Determine the iodine number of a fat from the following data obtained from an analysis:

Weight of fat taken....................	= 1.0214 grams
Quantity of iodine solution used........	= 25 c.c.
Thiosulphate, equivalent to iodine used (mean of 2 blank determinations).....	= 39.5 c.c.
Thiosulphate equivalent to remaining iodine..............................	= 13.4 c.c.
Thiosulphate equivalent to iodine absorbed..............................	= 26.1 c.c.

The thiosulphate solution is so standardized that 1 cubic centimeter of it is equivalent to .0122 gram of iodine.

(5) Describe the elaidin test.

(6) How is the presence of sesame oil in other vegetable oils detected?

(7) What tests would you apply to determine whether an oil is pure olive oil or not?

(8) What does the iodine number indicate in the analysis of fats?

(9) The refractive index of a fat at 33.5° is 1.4652; what is the refractive index at standard temperature (25°)?

(10) What determinations are made in the analysis of asphalt?

(11) State how the iodine number of a fat is determined.

(12) What does the saponification number indicate in the analysis of fats?

(13) How is the presence of hydrocarbons, as an adulterant in vegetable oils, detected?

(14) How would you determine the melting point of a fat?

(15) Describe Maumené's test.

(16) How is the cloud test performed on an illuminating oil?

(17) How is the flash test made?

(18) How is the acid number of an oil determined?

(19) What are drying oils?

(20) How is the specific gravity of a solid fat determined?

A KEY TO ALL THE QUESTIONS AND EXAMPLES

Contained in the Examination Questions Included in this Volume

The Keys that follow have been divided into sections corresponding to the Examination Questions to which they refer, and have been given corresponding section numbers. The answers and solutions have been numbered to correspond with the questions. When the answer to a question involves a repetition of statements given in the Instruction Paper, the reader has been referred to a numbered article, the reading of which will enable him to answer the question himself.

To be of the greatest benefit, the Keys should be used sparingly. They should be used much in the same manner as a pupil would go to a teacher for instruction with regard to answering some example he was unable to solve. If used in this manner, the Keys will be of great help and assistance to the student, and will be a source of encouragement to him in studying the various papers composing the course.

QUANTITATIVE ANALYSIS

(PART 4)

---

(1) ZnO contains 80.25 per cent. of zinc.

$.1505 \times .8025 = .12077625$ gram of zinc found

$$\frac{.12077625 \times 100}{.625} \doteq 19.32 \text{ per cent. of zinc.} \quad \text{Ans.}$$

(2) See Art. **36.**

(3) See Art. **47.**

(4) Fe_2O_3 contains 90 per cent. FeO; hence, $.225 \times .90 = .2025$ gram FeO found

$$\frac{.2025 \times 100}{1} = 20.25 \text{ per cent. } FeO. \quad \text{Ans.}$$

(5) $2{,}000 \times .90 = 1{,}800$ lb. of calcium carbonate. Calcium carbonate contains 56 per cent. lime; hence,

$1{,}800 \times .56 = 1{,}008$ lb. of lime. Ans.

(6) See Art. **2.**

(7) See Art. **3,** *et seq.*

(8) Feldspar is essentially a silicate of aluminum and potassium, with a smaller quantity of sodium, or of aluminum and sodium with a smaller quantity of potassium. Many samples also contain calcium, and generally smaller amounts of iron and magnesium.

(9) See Art. **7.**

(10) See Art. **10.**

(11) (*a*) and (*b*) See Art. **11.**

(12) See Art. **59.**

(13) (*a*) and (*b*) See Art. **24.**

(14) As the limestone contains 40 per cent. of carbon dioxide, 1 gram of it will contain $1 \times .40 = .4$ gram of carbon dioxide; 1,000 cubic centimeters (1 liter) of carbon dioxide weighs 1.97 grams; hence,

$$1.97 : .4 = 1{,}000 : x. \quad x = 203.05 \text{ c. c.} \quad \text{Ans.}$$

(15) See Arts. **19** to **22,** inclusive.

(16) See Art. **29.**

(17) (*a*) Zinc is present in the solution in the form of chloride, and as it is precipitated as sulphide, the chlorine set free unites with the hydrogen of the hydrogen sulphide, forming hydrochloric acid. Zinc sulphide is soluble in a solution containing any considerable amount of free hydrochloric acid, and enough acid may be formed during the reaction to prevent the complete precipitation of the zinc. If sodium acetate is now added, the hydrochloric acid unites with the sodium forming sodium chloride, and setting free acetic acid in which zinc sulphide is insoluble, and consequently the zinc will be completely precipitated.

(*b*) If enough sodium acetate is added to unite with all the hydrochloric acid, the nickel and cobalt will also be precipitated; hence, care must be taken to leave enough free hydrochloric acid in the solution to prevent the precipitation of these metals, and not enough to interfere with the precipitation of the zinc.

(18) See Art. **24,** *et seq.*

(19) See Art. **48.**

(20) See Art. **49.**

(21), (22), (23), (24), (25), (26), (27), (28) The percentage of the elements to be determined in the sample sent for analysis cannot be given, as it will vary somewhat from time to time. A careful record of the composition of each sample is kept, however, and the student will be graded upon the results.

QUANTITATIVE ANALYSIS

(PART 5)

---

(1) On the amount of iron it contains and its freedom from impurities. See Art. **2.**

(2) Silicon, sulphur, phosphorus, and manganese. Sometimes graphite, and more rarely total and combined carbon.

(3) See Arts. **56** and **60.**

(4) See Art. **28.**

(5) (*a*) To remove hydrochloric acid from the CO_2 evolved.
(*b*) See Art. **63.**

(6) See Art. **67.**

(7) See Art. **3.**

(8) (*a*) and (*b*) See Art. **3.**

(9) As an indicator. As soon as the iodine has decomposed all the hydrogen sulphide, with the formation of hydriodic acid, it begins to unite with the starch, forming blue starch iodide, and thus indicating that the reaction is complete.

(10) (*a*) See Art. **71.**
(*b*) See Art. **69.**

(11) (*a*) and (*b*) See Art. **15.**

(12) $$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

(13) See Art. **54.**

(14) See Art. **52,** *et seq.*

(15) See Art. **10.**

(16) $$H_2S + 2I = 2HI + S$$

(17) See Art. **61.**

(18)

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + 2KHSO_4 + H_2SO_4$$

(19) See Art. **58.**

(20) See Art. **59.**

(21) See Art. **74.**

QUANTITATIVE ANALYSIS

(PART 6)

---

(1) See Art. **9.**

(2) See Art. **10.**

(3) See Art. **44.**

(4) Multiply by .058318. See Art. **10**

(5) See Art. **45.**

(6) See Art. **11.**

(7) Albuminoid ammonia does not exist in water as ammonia, but is in the form of nitrogenous organic matter, which is broken up when boiled with potassium hydroxide and permanganate, yielding an amount of ammonia proportional to the amount of nitrogenous matter in the water.

(8) On the relative affinity of silver for chlorine and chromic acid. When silver nitrate is added to water containing both a chloride and a chromate, the silver unites with the chloride until all the chlorine is combined with silver. Any silver nitrate added after this reacts with the chromate, forming red silver chromate. The appearance of this red compound shows when enough silver nitrate has been added to react with all the chloride. See Art. **16.**

(9) (*a*) and (*b*) See Art. **1.**

(10) See Art. **17.**

(11) See Art. **43.**

(12) See Art. **12.**

(13) See Art. **54.**

(14) See Art. **1.**

(15) See Arts. **21** and **22.**

(16) See Art. **55.**

(17) See Art. **1.**

(18) (*a*) and (*b*) See Art. **24.**

(19) Pink. See Art. **38.**

(20) See Art. **66.**

QUANTITATIVE ANALYSIS

(PART 7)

(1) $\frac{11.2 \times 273 \times 771}{(273+22) \times 760} = 10.52+$ liters. Ans.

(2) See Art. **29.**

(3) See Arts. **70** and **71.**

(4) See Art. **36,** *et seq.*

(5) See Art. **2.**

(6) See Art. **29.**

(7) See Art. **9.**

(8) Substituting in formula **5** we obtain

$$\frac{100 \times 12 \times (767-11.2)}{760 \times (354.33 \times 2) \times (1+.00366 \times 13)} = 1.607 \text{ grams;}$$

and as the specific gravity of the sample is 1.021, 100 c. c. weighs 102.1 grams and the percentage of urea is

$$\frac{1.607 \times 100}{102.1} = 1.573. \quad \text{Ans.}$$

(9) Substituting in formula **4,** we obtain

$$\frac{97 \times (765-10.5) \times 273}{760 \times (273+12)} = 92.24+ \text{ c. c.} \quad \text{Ans.}$$

(10) See Art. **58.**

(11) See Art. **50.**

(12) See Art. **11.**

(13) See Arts. **59** and **60.**

(14) See Art. **64,** *et seq.*

(15) As 50 cubic centimeters of gas is taken, and this contains 20 per cent. of CO_2, the amount of CO_2 in each determination is .01977 gram. The reaction with the KOH is represented by the equation $2KOH + CO_2 = K_2CO_3 + H_2O$. Hence, 44 parts of CO_2 is absorbed by 112 parts KOH. Then,

$$44 : 112 = .01977 : x$$

$x = .05032$ gram KOH for each determination; $.05032 \times 600 = 30.192$ grams KOH for 600 determinations. Ans.

(16) See Arts **59** and **60.**

(17) See Art. **51.**

(18) See Art. **38.**

QUANTITATIVE ANALYSIS

(PART 8)

(1) See Art. **55.**

(2) Subacetate of lead is generally used. See Art. **99.**

(3) See Art. **50.**

(4) Substituting in formula **2,** we get

$$R = \frac{100 \times (86 + 19)}{142.66 - 13.5} = 81.29\% \text{ cane sugar. Ans.}$$

(5) See Art. **7.**

(6) See Art. **109.**

(7) See Art. **70.**

(8) It varies from 1.028 to 1.034. Average about 1.0319 See Arts. **10** and **11.**

(9) 26.048 grams pure cane sugar. See Art. **98.**

(10) See Art. **58.**

(11) See Art. **45.**

(12) See Arts. **106, 107,** and **108.**

(13) See Art. **22.**

(14) See Art. **42,** *et seq.*

(15) Substituting in formula **1,** we get

$$t = \left[\frac{100\times 1.0328-(2.56\times 1.0328)}{100-(1.0753\times 2.56\times 1.0328)}-1\right][250-(2.5\times 2.56)]$$

$$= 8.720 = \text{total solids not fat.}$$

Hence, $8.72+2.56 = 11.28\%$. Ans.

(16) See Art. **72.**

(17) See Art. **110.**

(18) We first calculate the percentage of cane sugar by substituting in formula **2,**

$$R = \frac{100\times(69+24)}{142.66-11} = 70.636\% \text{ cane sugar.}$$

For the calculation of the invert sugar, we have to calculate the proportion $R : I$, and the value of Z, in order to get the value of F, which is needed in formula **3.** The known values are $Cu = .315$, $W = 3.5$, and the percentage of cane sugar (polarization) $P = 70.636$.

$$\frac{Cu}{2} = \frac{.315}{2} = .1575 = Z. \quad Z\times\frac{100}{W} = .1575\times\frac{100}{3.5} = 4.5 = x$$

$$\frac{100\,P}{P+x} = \frac{7{,}063.6}{70.636+4.5} = 94.01 = R$$

$$100-R = 100-94.07 = 5.99 = I$$

$$R : I = 94.01 : 5.99$$

By consulting Table IV, we find that the vertical column headed "$I = 150$" is nearest to Z (= .1575), and the horizontal column 94 : 6 is nearest to the ratio $R : I$ (94.01 : 5.99). Where these two columns meet, we find the factor 51.6, and can now apply formula **3.**

$$\frac{Cu\,F}{W} = \frac{.315\times 51.6}{3.5} = 4.644\% \text{ invert sugar.}$$

Hence, the sample contains 70.636% cane sugar and 4.644% invert sugar. Ans.

(19) See Art. **111.**

(20) No. See Art. **10.**

QUANTITATIVE ANALYSIS

(PART 9)

(1) Substituting in formula **2,** we get

$$C = \frac{100 \times 15 - 135^\circ}{86.5} = 1.734\% \text{ ceresin in sample.} \quad \text{Ans.}$$

(2) As 1 cubic centimeter of the arsenious solution corresponds to .0033 gram of chlorine, 47.4 cubic centimeters corresponds to $47.4 \times .0033 = .15642$ gram in 50 cubic centimeters of the solution; but 50 cubic centimeters contains .575 gram of bleaching powder, hence the substance contains

$$\frac{.15642 \times 100}{.575} = 27.2\% \text{ available chlorine.} \quad \text{Ans.}$$

(3) See Art. **13.**

(4) The percentage of iodine absorbed equals

$$\frac{26.1 \times .0122 \times 100}{1.0214} = 31.174$$

which is the iodine number of the fat. Ans.

(5) See Art. **25.**

(6) See Art. **45.**

(7) See Arts. **37** and **38.**

(8) The iodine number in a fat analysis represents the quantity of iodine that the fat is able to absorb, and then serves as a measure of the unsaturated acids present. See Art. **8,** *et seq.*

(9) See Art. **31.** $33.5 - 25 = 8.5$; $.000176 \times 8.5 = .0015$, nearly. Then $1.4652 + .0015 = 1.4667$, refractive index at standard temperature. Ans.

(10) See Art. **2.**

(11) See Arts. **11** and **12.**

(12) It indicates the number of milligrams of potassium hydrate required to saponify 1 gram of the fat, and, therefore, represents the capacity of saturation of the fatty acids present. See Art. **8.**

(13) See Art. **34.**

(14) See Art. **57.**

(15) See Art. **26.**

(16) See Art. **71.**

(17) See Arts. **72, 73,** and **74.**

(18) See Art. **14.**

(19) See Art. **20.**

(20) See Art. **29.**

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NOTE.—All items in this index refer first to the section and then to the page of the section. Thus, "Absolute water 28 23" means that absolute water will be found on page 23 of section 28.

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